Scott correction for large atoms and molecules in a self-generated magnetic field

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Abstract

We consider a large neutral molecule with total nuclear charge Z in non-relativistic quantum mechanics with a self-generated classical electromagnetic field. To ensure stability, we assume that $Z\alpha^2 \le \kappa_0$ for a sufficiently small κ_0, where α denotes the fine structure constant. We show that, in the simultaneous limit $Z \to \infty$, $\alpha \to 0$ such that $\kappa = Z\alpha^2$ is fixed, the ground state energy of the system is given by a two term expansion $c_1 Z^{7/3} + c_2(\kappa)Z^2 + o(Z^2)$. The leading term is given by the non-magnetic Thomas-Fermi theory. Our result shows that the magnetic field affects only the second (so-called Scott) term in the expansion.

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1 Introduction and the main result

We introduce the molecular many-body Hamiltonian of N dynamical electrons and M static nuclei in three space dimensions. The electron coordinates are $x_1, x_2, \dots, x_N \in \mathbb{R}^3$, the nuclei are located at $\mathbf{R} = (R_1, R_2, \dots, R_M) \in \mathbb{R}^{3M}$. Let $\mathbf{Z} = (Z_1, Z_2, \dots, Z_M)$ denote the nuclear charges, $Z_j > 0$, with total nuclear charge $Z = \sum_{k=1}^M Z_k$. We assume that the system is neutral, i.e. $N = Z$, in particular Z is integer. The electrons are subject to a self-generated magnetic field, $B = \nabla \times A$, where $A \in H^1(\mathbb{R}^3, \mathbb{R}^3)$ is a magnetic vector potential. The magnetic field energy is

$$\frac{1}{8\pi\alpha^2}\int_{\mathbb{R}^3} B^2 = \frac{1}{8\pi\alpha^2}\int_{\mathbb{R}^3} |\nabla \times A|^2,$$

where α is the fine structure constant.

In the non-relativistic approximation, the kinetic energy operator of the j-th particle is given by the magnetic Schrödinger or the Pauli operator,

$$T^{(j)}(A) = (-i\nabla_{x_j} + A(x_j))^2, \quad \text{or} \quad T^{(j)}(A) = \big[\boldsymbol{\sigma}\cdot(-i\nabla_{x_j} + A(x_j))\big]^2, \tag{1.1}$$

depending on whether the particles are considered spinless or have spin-$\frac{1}{2}$. Here $\boldsymbol{\sigma} = (\sigma_1, \sigma_2, \sigma_3)$ is the vector of Pauli matrices. The Schrödinger operator acts on the space $L^2(\mathbb{R}^3)$, the Pauli operator acts on $L^2(\mathbb{R}^3, \mathbb{C}^2)$. We will work with the Pauli operator, the treatment of the magnetic Schrödinger operator is simpler and we will only comment on the modifications needed.

The electrostatic potential of the electrons is the difference of the nuclear attraction

$$V(\mathbf{Z}, \mathbf{R}, x) = \sum_{k=1}^M \frac{Z_k}{|x - R_k|},$$

and electron-electron repulsion

$$\sum_{1\le i<j\le N} \frac{1}{|x_i - x_j|}.$$

The total energy of the electrons is given by the Hamiltonian

$$H_N(\mathbf{Z}, \mathbf{R}, A) := \sum_{j=1}^N \big[T^{(j)}(A) - V(\mathbf{Z}, \mathbf{R}, x_j)\big] + \sum_{1\le i<j\le N} \frac{1}{|x_i - x_j|}. \tag{1.2}$$

This operator acts on the space of antisymmetric functions $\bigwedge_1^N \mathcal{H}$, where $\mathcal{H} = L^2(\mathbb{R}^3) \otimes \mathbb{C}^2$ is the single particle Hilbert space.

For a given vector potential A, the ground state energy of the electrons is given by

$$E(\mathbf{Z}, \mathbf{R}, A) := \inf \mathrm{Spec}\, H_N(\mathbf{Z}, \mathbf{R}, A) \tag{1.3}$$

with $N = Z = \sum_k Z_k$. By gauge invariance, $E(\mathbf{Z}, \mathbf{R}, A)$ depends only on the magnetic field $B = \nabla \times A$. Considering the magnetic field dynamical, we focus on the absolute ground state energy of the system, that includes the field energy,

$$E(\mathbf{Z}, \mathbf{R}, A) + \frac{1}{8\pi\alpha^2} \int_{\mathbb{R}^3} |\nabla \times A|^2, \tag{1.4}$$

and we will minimize over all vector potentials.

Since we are interested in gauge invariant quantities (like energy, ground state density), we can always choose a divergence free gauge, $\nabla \cdot A = 0$. In this case, the field energy is given by

$$\frac{1}{8\pi\alpha^2} \int_{\mathbb{R}^3} |\nabla \times A|^2 = \frac{1}{8\pi\alpha^2} \int_{\mathbb{R}^3} |\nabla \otimes A|^2. \tag{1.5}$$

Since the magnetic energy will always be finite, we can also assume that $A \in L^6(\mathbb{R}^3)$ (see Appendix of [FLL] for the existence of such a gauge), and we thus have

$$\nabla \cdot A = 0, \qquad \Big(\int_{\mathbb{R}^3} A^6 \Big)^{1/3} \le C \int_{\mathbb{R}^3} |\nabla \otimes A|^2 = \int_{\mathbb{R}^3} |\nabla \times A|^2 \tag{1.6}$$

by the Sobolev inequality.

We will call a vector potential A *admissible* if $A \in L^6(\mathbb{R}^3)$, $\nabla \otimes A \in L^2(\mathbb{R}^3)$, and $\nabla \cdot A = 0$. For admissible vector potentials, the total energy is

$$\mathcal{E}(\mathbf{Z}, \mathbf{R}, A, \alpha) := E(\mathbf{Z}, \mathbf{R}, A) + \frac{1}{8\pi\alpha^2} \int_{\mathbb{R}^3} |\nabla \otimes A|^2,$$

and the absolute ground state energy of the system is given by

$$E_{\mathrm{abs}}(\mathbf{Z}, \mathbf{R}, \alpha) := \inf_A \Big\{ \mathcal{E}(\mathbf{Z}, \mathbf{R}, A, \alpha) \Big\}, \tag{1.7}$$

where the infimum is taken over all admissible vector potentials A.

Our units are $\hbar^2(2me^2)^{-1}$ for the length, $2me^4\hbar^{-2}$ for the energy and $2mec\hbar^{-1}$ for the magnetic vector potential, where m is the electron mass, e is the electron charge and $\hbar$ is the Planck constant. In these units, the only physical parameter that appears in the total Hamiltonian (1.4) is the dimensionless fine structure constant $\alpha = e^2(\hbar c)^{-1} \sim \frac{1}{137}$. We will assume that $\max_k Z_k\alpha^2 \le \kappa_0$ with some sufficiently small universal constant $\kappa_0 \le 1$ and we will investigate the simultaneous limit $Z \to \infty$, $\alpha \to 0$.

The main result of this paper is:

Theorem 1.1. *Fix $M \in \mathbb{N}$. Let $\mathbf{z} = (z_1, z_2, \ldots, z_M)$ with $z_1, z_2, \ldots, z_M > 0$, $\sum_{k=1}^M z_k = 1$, and $\mathbf{r} = (r_1, r_2, \ldots, r_M) \in \mathbb{R}^{3M}$ with $\min_{k\neq\ell} |r_k - r_\ell| \geq r_{min}$ for some $r_{min} > 0$ be given. With a positive real parameter $Z > 0$, define $\mathbf{Z} = (Z_1, Z_2, \ldots, Z_M)$, $Z_k := Z z_k$, and $\mathbf{R} = Z^{-1/3}\mathbf{r}$ to be the charges and the locations of the nuclei. Then there exists a constant $E^{\mathrm{TF}}(\mathbf{z}, \mathbf{r})$ and a universal (independent of $\mathbf{z}, \mathbf{r}$ and M), monotonically decreasing function $S : (0, \kappa_0] \to \mathbb{R}$ with some universal $\kappa_0 > 0$ and with $\lim_{\kappa\to 0+} S(\kappa) = \frac{1}{8}$ such that as $Z = \sum_{k=1}^M Z_k \to \infty$, $\alpha \to 0$ with $\max_k 8\pi Z_k\alpha^2 \leq \kappa_0$, we have*

$$E_{\mathrm{abs}}(\mathbf{Z}, \mathbf{R}, \alpha) = Z^{7/3} E^{\mathrm{TF}}(\mathbf{z}, \mathbf{r}) + 2Z^2 \sum_{k=1}^{M} z_k^2 S(8\pi Z_k \alpha^2) + o(Z^2). \tag{1.8}$$

Remark 1.2. *The constant $E^{\mathrm{TF}}(\mathbf{z}, \mathbf{r})$ is given by the Thomas-Fermi theory for nonrelativistic molecules without magnetic field, see below. The factor 2 in the Scott term is due to the spin degeneracy.*

Remark 1.3. *Our current proof does not provide an effective error term in (1.8) although we conjecture that $o(Z^2)$ can be replaced with $O(Z^{2-\eta})$ with some $\eta > 0$ where the constant in the error term depends only on r_{min} and M.*

Remark 1.4. *From the monotonicity of $E_{\mathrm{abs}}(\mathbf{Z}, \mathbf{R}, \alpha)$ in α, it is obvious that the function S is monotonically decreasing. It is known that there is a finite critical constant $\kappa_{cr} > 0$ such that the system is unstable if $\max_k Z_k\alpha^2 > \kappa_{cr}$, in particular the restriction $\max_k Z_k\alpha^2 \leq \kappa_0$ in the theorem is necessary but our threshold κ_0 is not optimal. We conjecture that $S(\kappa)$ is a strictly decreasing function, but unfortunately our proof does not provide this statement. In fact, we even cannot exclude the possibility that $S(\kappa)$ is constant (=1/8) for all κ up to the critical value κ_{cr} beyond which it is minus infinity.*

Remark 1.5. *An energy expansion similar to (1.8) was derived in a relativistic model (without magnetic fields) in [SSS]. In the relativistic case one must also consider simultaneous limits $Z \to \infty$, $\alpha \to 0$. In this case, however, it is the combination $Z_k\alpha$ which must remain bounded in contrast to Theorem 1.1, where a bound on $Z_k\alpha^2$ is required. In the atomic case, $M = 1$, an alternative proof of the relativistic energy asymptotics was given in [FSW1].*

The scaling can be understood from Thomas-Fermi theory which we recall briefly [LS, L]. Let $0 \leq \varrho(x) \in L^{5/3}(\mathbb{R}^3) \cap L^1(\mathbb{R}^3)$ then the Thomas-Fermi energy functional is defined as

$$\mathcal{E}^{\mathrm{TF}}(\varrho) := \frac{3}{5}(3\pi^2)^{2/3} \int_{\mathbb{R}^3} \varrho^{5/3} - \int_{\mathbb{R}^3} V(\mathbf{z}, \mathbf{r}, x)\varrho(x)\mathrm{d}x + D(\varrho)$$

with

$$D(\varrho) := D(\varrho, \varrho) := \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\varrho(x)\varrho(y)}{|x - y|} \mathrm{d}x\mathrm{d}y$$

(the coefficient in front of the kinetic energy takes into account the spin degeneracy). It is well known that the variational problem

$$\inf\Big\{\mathcal{E}^{\mathrm{TF}}(\varrho)\ :\ \varrho\in L^1(\mathbb{R}^3)\cap L^{5/3}(\mathbb{R}^3),\ \ \int\varrho=\sum_{k=1}^{M}z_k\Big\} \tag{1.9}$$

has a unique, strictly positive minimizer, called the *Thomas-Fermi density* and denoted by $\varrho^{\mathrm{TF}}(x)=\varrho^{\mathrm{TF}}(\mathbf{r},\mathbf{z},x)$. The value of the minimum, $E^{\mathrm{TF}}(\mathbf{z},\mathbf{r}):=\mathcal{E}^{\mathrm{TF}}(\varrho^{\mathrm{TF}})$, is called the *Thomas-Fermi energy*. The function

$$V^{\mathrm{TF}}(\mathbf{z},\mathbf{r},x):=V(\mathbf{z},\mathbf{r},x)-\varrho^{\mathrm{TF}}*|x|^{-1} \tag{1.10}$$

is called the *Thomas-Fermi potential*; it is strictly positive and it solves the Thomas-Fermi equation

$$V^{\mathrm{TF}}_{\mathbf{z},\mathbf{r}}=(3\pi^2)^{2/3}\big[\varrho^{\mathrm{TF}}_{\mathbf{z},\mathbf{r}}\big]^{2/3}. \tag{1.11}$$

Sometimes we will use the notation $V^{\mathrm{TF}}_{\mathbf{z},\mathbf{r}}(x)$ instead of $V^{\mathrm{TF}}(\mathbf{z},\mathbf{r},x)$ and likewise for $\varrho^{\mathrm{TF}}_{\mathbf{z},\mathbf{r}}$. The key quantities in the Thomas-Fermi theory have the following scaling behavior:

$$\begin{aligned} V^{\mathrm{TF}}(\mathbf{z},\mathbf{r},x)&=h^{-4}V^{\mathrm{TF}}(h^3\mathbf{z},h^{-1}\mathbf{r},h^{-1}x)\\ \varrho^{\mathrm{TF}}(\mathbf{z},\mathbf{r},x)&=h^{-6}\varrho^{\mathrm{TF}}(h^3\mathbf{z},h^{-1}\mathbf{r},h^{-1}x)\\ E^{\mathrm{TF}}(\mathbf{z},\mathbf{r})&=h^{-7}E^{\mathrm{TF}}(h^3\mathbf{z},h^{-1}\mathbf{r}) \end{aligned} \tag{1.12}$$

for any $h>0$. We also note that the Thomas-Fermi energy defined as the minimal value of (1.9) can also be given by the phase-space integral of the classical symbol with the Thomas-Fermi potential, i.e.

$$E^{\mathrm{TF}}(\mathbf{z},\mathbf{r}):=2\frac{1}{(2\pi)^3}\int_{\mathbb{R}^3\times\mathbb{R}^3}[p^2-V^{\mathrm{TF}}_{\mathbf{z},\mathbf{r}}(q)]_-\mathrm{d}p\mathrm{d}q-D(\varrho^{\mathrm{TF}}_{\mathbf{z},\mathbf{r}}), \tag{1.13}$$

where $[a]_-=-\min\{a,0\}$ denotes the negative part of a real number or a selfadjoint operator. The factor 2 in (1.13) accounts for the spin degeneracy.

Suppose we replace the many-body electrostatic potential in $H_N(\mathbf{Z},\mathbf{R},A)$ by its mean field approximation as

$$-\sum_{j=1}^{N}V(\mathbf{Z},\mathbf{R},x_j)+\sum_{1\le i<j\le N}\frac{1}{|x_i-x_j|}\approx -V^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}}(x_j)-D(\varrho^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}}).$$

Then the absolute ground state energy $E_{\mathrm{abs}}(\mathbf{Z},\mathbf{R},\alpha)$ will be approximated by

$$\begin{aligned} &\inf_A\Big\{\mathrm{Tr}\,\big[T(A)-V^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}}\big]_-+\frac{1}{8\pi\alpha^2}\int_{\mathbb{R}^3}|\nabla\otimes A|^2-D(\varrho^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}})\Big\} \\ &\qquad\approx Z^{4/3}\inf_A\Big\{\mathrm{Tr}\,\big[T_h(A)-V^{\mathrm{TF}}_{\mathbf{z},\mathbf{r}}\big]_-+\frac{1}{8\pi Z\alpha^2}h^{-2}\int_{\mathbb{R}^3}|\nabla\otimes A|^2\Big\}-Z^{7/3}D(\varrho^{\mathrm{TF}}_{\mathbf{z},\mathbf{r}}), \end{aligned} \tag{1.14}$$

by using the scaling property (1.12) with the choice $h = Z^{-1/3}$ and introducing the notation

$$T_h(A) = [\boldsymbol{\sigma} \cdot (-ih\nabla + A)]^2.$$

The infimum in (1.14) is taken over all admissible vector potentials A, but in fact taking infimum over slightly different sets yields the same result, see a more detailed discussion in Appendix A of [EFS1].

Note that the trace in (1.14) is computed in the spinor space $L^2(\mathbb{R}^3, \mathbb{C}^2)$. Any operator $\mathcal{M}$ acting on $L^2(\mathbb{R}^3)$ will be naturally identified with $\mathcal{M} \otimes I$ acting on the spinor space $L^2(\mathbb{R}^3) \otimes \mathbb{C}^2$ and we will not distinguish between $\mathcal{M}$ and $\mathcal{M} \otimes I$ in the notation. This will not cause any confusion but we need to keep in mind that $\mathrm{Tr}_{\,L^2(\mathbb{R}^3)\otimes\mathbb{C}^2}\mathcal{M} = 2\mathrm{Tr}_{\,L^2(\mathbb{R}^3)}\mathcal{M}$. Unless indicated otherwise, the traces in this paper are computed on $L^2(\mathbb{R}^3) \otimes \mathbb{C}^2$.

We thus reduced the problem to a semiclassical analysis of the Pauli operator with a self-generated magnetic field. The leading term in the asymptotic expansion in negative powers of $h = Z^{-1/3}$ for the one particle energy in (1.14) is given by the Weyl term

$$\begin{aligned}\inf_A \Big\{ \mathrm{Tr}\, \big[T_h(A) - V^{\mathrm{TF}}_{\mathbf{z},\mathbf{r}}\big]_- + \frac{1}{\kappa h^2} \int_{\mathbb{R}^3} |\nabla \otimes A|^2 \Big\} \\ = h^{-3} \frac{2}{(2\pi)^3} \int_{\mathbb{R}^3 \times \mathbb{R}^3} [p^2 - V^{\mathrm{TF}}_{\mathbf{z},\mathbf{r}}(q)]_- \mathrm{d}p\mathrm{d}q + o(h^{-3})\end{aligned} \tag{1.15}$$

as long as $\kappa := 8\pi Z\alpha^2 \le \kappa_0$ with some sufficiently small fixed positive κ_0 (in fact, it is sufficient that $\max_k 8\pi Z_k\alpha^2 \le \kappa_0$). Notice that the leading term does not depend on κ. Via (1.13) this produces the leading term asymptotics $Z^{7/3}E^{\mathrm{TF}}(\mathbf{z}, \mathbf{r}) + o(Z^{7/3})$ for the many body ground state energy.

A fundamental result of Lieb and Simon [LS] (see also [L]) rigorously justified this heuristics without magnetic field and with an effective error term. Thus they proved the leading term asymptotics in (1.8) for the ground state energy of large atoms and molecules without magnetic field. The next order term, known as the Scott correction, is of order Z^2. For the non-magnetic case it is explicitly given by

$$2 \cdot \frac{Z^2}{8} \sum_{k=1}^{M} z_k^2 \tag{1.16}$$

(the additional factor 2 is due to the spin degeneracy) and it was rigorously proved for atoms in [H, SW1] and for molecules in [IS] (see also [SW2, SW3, SS]). The next term in the expansion of order $Z^{5/3}$ was obtained in [FS].

It was established in [ES3] that the inclusion of a self-generated magnetic field does not change the leading term asymptotics in (1.8). The main theorem in this paper, Theorem 1.1 shows that the effect of the magnetic field appears in the second (Scott) term in the asymptotic expansion.

The proof has two main steps. First we reduce the interacting many-body problem to an effective one-body semiclassical problem as it was described in (1.14). This step will be done

rigorously in Section 3. The second step is an accurate second order semiclassical asymptotics for the magnetic problem. More precisely, we will show the following more accurate version of (1.15):

$$\inf_A \Big\{ \mathrm{Tr}\, \big[T_h(A) - V^{\mathrm{TF}}_{\mathbf{z},\mathbf{r}}\big]_- + \frac{1}{\kappa h^2}\int_{\mathbb{R}^3} |\nabla \otimes A|^2 \Big\} \tag{1.17}$$
$$= h^{-3}\frac{2}{(2\pi)^3}\int_{\mathbb{R}^3\times\mathbb{R}^3} [p^2 - V^{\mathrm{TF}}_{\mathbf{z},\mathbf{r}}(q)]_- \mathrm{d}p\mathrm{d}q + 2h^{-2}\sum_{k=1}^M z_k^2 S(8\pi Z_k\alpha^2) + o(h^{-2}),$$

with $\kappa = 8\pi Z\alpha^2$ and under the assumption that $\max_k 8\pi Z_k\alpha^2 \le \kappa_0$ with some κ_0 that is sufficiently small. Together with (1.13), (1.14) and $h = Z^{-1/3}$, (1.17) will yield (1.8).

The precise second order semiclassical expansion for

$$\inf_A \Big\{ \mathrm{Tr}\, \big[T_h(A) - V\big]_- + \frac{1}{\kappa h^2}\int_{\mathbb{R}^3} |\nabla \otimes A|^2 \Big\} \tag{1.18}$$

is of interest itself for a general potential V and with $\kappa \le \kappa_0$. Under general conditions on V the leading term is given by the classical Weyl term as in (1.15). A local version of this statement was proven in Theorem 1.3 of [ES3] (this theorem contains only the lower bound, the upper bound is trivial). The global version was given in Theorem 2.2 of [EFS1], where the condition $\kappa \le \kappa_0$ could even be relaxed to $\kappa = o(h^{-1})$.

The subleading term in the expansion for (1.18) depends on the singularity structure of the potential. For $V \in C_0^\infty$ we proved in Theorem 1.1 of [EFS2] that the Weyl asymptotics holds with an error $O(h^{-2+\eta})$. The main ingredient was a local semiclassical asymptotics that we recall in Theorem 2.2.

Using this result for smooth potentials and a multiscale analysis, we will show in Section 2 that for potentials with Coulomb singularities, a non-zero second order term arises from the non-semiclassical effects of the innermost shells of the Hydrogen-like atoms. The precise form of this term will not be as explicit as in the non-magnetic case, (1.16), but it will be given by a universal function S which we will describe in Theorem 2.4 and prove in Section 4.

2 Semiclassical results up to second order

In this section we are interested in noninteracting fermions, each is subject to the one-body Hamiltonian $H = T_h(A) - V$. The total ground state energy of the system is given by

$$\mathcal{E}(A) := \mathrm{Tr}\, \big[T_h(A) - V\big]_- + \frac{1}{\kappa h^2}\int_{\mathbb{R}^3} |\nabla \times A|^2 = \mathrm{Tr}\, \big[T_h(A) - V\big]_- + \frac{1}{\kappa h^2}\int_{\mathbb{R}^3} |\nabla \otimes A|^2, \tag{2.1}$$

where $\kappa > 0$ is a parameter, and where the last equality uses that $\nabla \cdot A = 0$ which can be assumed by gauge invariance.

We will assume that the potential has a multiscale structure. Intuitively, this means that there exist two scaling functions, $f, \ell : \mathbb{R}^3 \to \mathbb{R}_+$ such that for any $u \in \mathbb{R}^3$, within the ball $B_u(\ell(u))$ centered at u with radius $\ell(u)$, the size of V is of order $f^2(u)$ and V varies on scale $\ell(u)$. Moreover, we also require that the continuous family of balls $B_u(\ell(u))$ supports a regular partition of unity. The following lemma states this condition precisely. This statement was proved in Theorem 22 of [SS] with an explicit construction[1].

We will use the notation $B_x(r)$ for the ball of radius r and center at x and if $x = 0$, we use $B(r) = B_0(r)$.

Lemma 2.1 ([SS, Theorem 22])**.** *Fix a cutoff function $\psi \in C_0^\infty(\mathbb{R}^3)$ supported in the unit ball $B(1)$ satisfying $\int \psi^2 = 1$. Let $\ell : \mathbb{R}^3 \to (0,1]$ be a C^1 function with $\|\nabla \ell\|_\infty < 1$. Let $J(x,u)$ be the Jacobian of the map $u \mapsto (x-u)/\ell(u)$ and we define*

$$\psi_u(x) = \psi\Big(\frac{x-u}{\ell(u)}\Big)\sqrt{J(x,u)}\ell(u)^{3/2}.$$

Then, for all $x \in \mathbb{R}^3$,

$$\int_{\mathbb{R}^3} \psi_u(x)^2 \ell(u)^{-3} \mathrm{d}u = 1, \tag{2.2}$$

and for all multi-indices $n \in \mathbb{N}^3$ we have

$$\|\partial^n \psi_u\|_\infty \le C_n \ell(u)^{-|n|}, \qquad |n| = n_1 + n_2 + n_3, \tag{2.3}$$

where C_n depends on the derivatives of ψ but is independent of u. □

We will require that the potential satisfies

$$|\partial^n V(u)| \le C_n f(u)^2 \ell(u)^{-|n|} \tag{2.4}$$

for all $n \in \mathbb{N}^3$ uniformly in u in some domain $\Omega \subset \mathbb{R}^3$. In applications, Ω will exclude an h-neighborhood of the core of the Coulomb potentials. For brevity, we will often use $\ell_u = \ell(u)$ and $f_u = f(u)$.

Inserting the partition of unity (2.2), by IMS formula and reallocation of the localization error, we have

$$\begin{aligned} \mathcal{E}(A) =& \mathrm{Tr}\,\Big[\int_{\mathbb{R}^3} \frac{\mathrm{d}u}{\ell_u^3}\Big(\psi_u[T_h(A) - V]\psi_u - h^2|\nabla\psi_u|^2\Big)\Big]_- + \frac{1}{\kappa h^2}\int_{\mathbb{R}^3} |\nabla \otimes A|^2 \\ \ge& \mathrm{Tr}\,\Big[\int_{\mathbb{R}^3} \frac{\mathrm{d}u}{\ell_u^3}\psi_u\big[T_h(A) - V - Ch^2|\nabla\psi_u|^2\big]\psi_u\Big]_- + \frac{1}{\kappa h^2}\int_{\mathbb{R}^3} |\nabla \otimes A|^2 \\ \ge& \int_{\mathbb{R}^3} \frac{\mathrm{d}u}{\ell_u^3}\mathcal{E}(A, V_u^+, \psi_u), \end{aligned} \tag{2.5}$$

[1] Multiscaling was introduced in semiclassical problems in [IS] (see also [Sob, Sob1])

where

$$V_u^+ := V + Ch^2|\nabla\psi_u|^2$$

and

$$\mathcal{E}(A, V_u^+, \psi_u) := \mathrm{Tr}\,\Big[\psi_u[T_h(A) - V_u^+]\psi_u\Big]_- + \frac{1}{\kappa h^2}\int_{\mathbb{R}^3}\psi_u^2|\nabla\otimes A|^2.$$

In (2.5) we used $\mathrm{Tr}\,[\int O_u \mathrm{d}u]_- \geq \int \mathrm{Tr}\,[O_u]_- \mathrm{d}u$ for any continuous family of operators O_u.

We will assume that V_u^+ satisfies the same bound (2.4) as V, i.e.

$$h \leq C f_u \ell_u. \tag{2.6}$$

For the Coulomb-like singularity, $V(x) = 1/|x|$, we will choose the $\ell(u) = c|u|$ with some $c < 1$ and $f_u = \ell_u^{-1/2}$ so that (2.4) holds. With this choice (2.6) holds for $|u| \geq Ch^2$, so the multiscale analysis will work apart from a very small neighborhood of the nucleus.

Next we recall our local semiclassical result from [EFS2] on a model problem living in the ball $B(\ell)$ of radius $\ell > 0$.

Theorem 2.2 (Semiclassical asymptotics [EFS2, Theorem 3.1])**.** *There exist universal constants $n_0 \in \mathbb{N}$ and $\varepsilon > 0$ such that the following is satisfied. Let $\kappa_0, f, \ell, h_0 > 0$ and let $\kappa \leq \kappa_0 f^{-2}\ell^{-1}$. Let $\psi \in C_0^\infty(\mathbb{R}^3)$ with $\mathrm{supp}\,\psi \in B(\ell)$ and let $V \in C^\infty(\overline{B}(\ell))$ be a real valued potential satisfying*

$$|\partial^n \psi| \leq C_n \ell^{-|n|}, \qquad |\partial^n V| \leq C_n f^2 \ell^{-|n|} \tag{2.7}$$

for every multiindex n with $|n| \leq n_0$. Then

$$\left|\inf_A \Big(\mathrm{Tr}\,[\psi H_h(A)\psi]_- + \frac{1}{\kappa h^2}\int_{B(2\ell)}|\nabla\otimes A|^2\Big) - 2(2\pi h)^{-3}\int_{\mathbb{R}^3\times\mathbb{R}^3}\psi(q)^2\big[p^2 - V(q)\big]_- \mathrm{d}q\mathrm{d}p\right| \leq Ch^{-2+\varepsilon}f^{4-\varepsilon}\ell^{2-\varepsilon} \tag{2.8}$$

for any $h \leq h_0 f\ell$. The constant C depends only on κ_0, h_0 and on the constants C_n, in (2.7). The factor 2 in front of the semiclassical term accounts for the spin and it is present only for the Pauli case. □

Remark. By variation of κ, we obtain from Theorem 2.2 the following estimate

$$\frac{1}{\kappa h^2}\int_{B(2\ell)}|\nabla\otimes A|^2 \leq Ch^{-2+\varepsilon}f^{4-\varepsilon}\ell^{2-\varepsilon}, \tag{2.9}$$

for (near) minimizing vector potentials A.

The following result from [EFS2] can be viewed as a partial converse to (2.9) as it estimates the semiclassical error in terms of the magnetic field. Note that the assumption in (2.10) below is much weaker than (2.9).

Theorem 2.3 ([EFS2, Theorem 3.2])**.** *Let the assumptions be as in Theorem 2.2 and assume that A satisfies the bound*

$$\int_{B(2\ell)} |\nabla \otimes A|^2 \leq Ch^{-2} f^4 \ell^3. \tag{2.10}$$

Then, with ε from Theorem 2.2 we have

$$\begin{aligned} Ch^{-2} f^3 \ell^{3/2} \Big\{ \int_{B(2\ell)} |\nabla \otimes A|^2 \Big\}^{1/2} + Ch^{-1} f^3 \ell & \\ \geq \mathrm{Tr}\, [\psi H_h(A) \psi]_- - 2(2\pi h)^{-3} \int_{\mathbb{R}^3 \times \mathbb{R}^3} \psi(q)^2 \big[p^2 - V(q)\big]_- \mathrm{d}q \mathrm{d}p & \\ \geq Ch^{-2+\varepsilon} f^{4-\varepsilon} \ell^{2-\varepsilon} - Ch^{-2} f^2 \ell \int_{B(2\ell)} |\nabla \otimes A|^2, & \end{aligned} \tag{2.11}$$

where the constants may depend on h_0 and κ_0 and on the constant in (2.10)*.*

Very close to the nuclei (at a distance $h^3 \sim Z^{-1}$) the semiclassical approximation is no longer valid due to the local Coulomb singularity and the energy is given by a specific function S that describes the contribution of the innermost electrons. Since the nuclei are separated on the much larger semiclassical scale h, this effect is additive for different nuclei. Thus S can be defined via the Hydrogen atom. The following theorem defines S and gives some of its properties. It will be proven in Section 4.

Theorem 2.4. *Let $\phi \in C_0^\infty(\mathbb{R}^3)$ be a cutoff function with $\mathrm{supp}\, \phi \subset B(1)$, $\phi \equiv 1$ on $B(1/2)$ and such that $\widetilde{\phi} := (1-\phi^2)^{1/2} \in C^\infty(\mathbb{R}^3)$. Define $\phi_R(x) = \phi(x/R)$ for some $R > 0$. There is a universal critical constant $\kappa_{cr} > 0$ such that for any $\kappa < \kappa_{cr}$ and for any fixed $0 < \beta \leq (2\kappa)^{-1}$ the following limit exists, it is finite and it depends only on κ (and it is independent of the choice of ϕ and β satisfying the conditions listed above):*

$$\begin{aligned} \lim_{R\to\infty} \Bigg[\inf_A \Big\{ \mathrm{Tr}\, \Big[\phi_R \Big(T_{h=1}(A) - \frac{1}{|x|} \Big) \phi_R \Big]_- + \frac{1}{\kappa} \int_{B(R/4)} |\nabla \otimes A|^2 + \beta \int_{B(2R) \setminus B(R/4)} |\nabla \otimes A|^2 \Big\} & \\ - 2(2\pi)^{-3} \int_{\mathbb{R}^3 \times \mathbb{R}^3} \phi_R^2(q) \Big[p^2 - \frac{1}{|q|} \Big]_- \mathrm{d}p \mathrm{d}q \Bigg] =: 2S(\kappa). & \end{aligned} \tag{2.12}$$

The limit is denoted by $2S(\kappa)$ following the convention in the literature to indicate explicitly the factor 2 that accounts for the spin degeneracy. The function $S(\kappa)$ is defined on $[0, \kappa_{cr})$, it is decreasing and $S(0) = 1/8$, corresponding to the coefficient of the non-magnetic Scott correction.

Furthermore, there exists a sequence $\{A_R\}\subset H^1(\mathbb{R}^3)$ *with* $\operatorname{supp} A_R\subset B(R/4)$ *and such that*

$$\lim_{R\to\infty}\Bigg[\mathrm{Tr}\,\Big[\phi_R\Big(T_{h=1}(A_R)-\frac{1}{|x|}\Big)\phi_R\Big]_- +\frac{1}{\kappa}\int_{B(R/4)}|\nabla\otimes A_R|^2 \\ -2(2\pi)^{-3}\int_{\mathbb{R}^3\times\mathbb{R}^3}\phi_R^2(q)\Big[p^2-\frac{1}{|q|}\Big]_-\mathrm{d}p\mathrm{d}q\Bigg]=2S(\kappa). \quad (2.13)$$

This way of introducing a Scott correction when one cannot calculate its explicit value was introduced in [Sob] and was used later in [SS, SSS]. In the case of the relativistic Scott correction an alternative method of characterizing the Scott term was given in [FSW1, FSW2].

Equivalently, one could define $S(\kappa)$ via another limiting procedure, which may look more canonical:

Lemma 2.5. *For the function* $S(\kappa)$ *defined in* (2.12) *we have*

$$\lim_{\mu\to 0^+}\Bigg[\inf_A\Big\{\mathrm{Tr}\,\Big[T_{h=1}(A)-\frac{1}{|x|}+\mu\Big]_- +\frac{1}{\kappa}\int_{\mathbb{R}^3}|\nabla\otimes A|^2\Big\} \\ -2(2\pi)^{-3}\int_{\mathbb{R}^3\times\mathbb{R}^3}\Big[p^2-\frac{1}{|q|}+\mu\Big]_-\mathrm{d}p\mathrm{d}q\Bigg]=2S(\kappa). \quad (2.14)$$

In the main arguments of this paper we will always use the definition (2.12) and only in Section 6, with the help of the main semiclassical theorem, Theorem 2.7, we will prove Lemma 2.5.

Now we formulate the precise second order semiclassical asymptotics for a potential with Coulomb like singularities and with certain scaling properties that are satisfied by the Thomas-Fermi potential V^{TF}. We first specify the properties of V^{TF} that are used in the proof.

For any given $\mathbf{r}=(r_1,r_2,\ldots,r_M)\in\mathbb{R}^{3M}$ and $\mathbf{z}=(z_1,z_2,\ldots,z_M)\in\mathbb{R}^M_+$ set

$$r_{min}:=\min_{k\neq\ell}|r_k-r_\ell|$$

$$d(x):=\min\{|x-r_k|\;:\;k=1,2,\ldots,M\}$$

and

$$f(x):=\min\{d(x)^{-1/2},d(x)^{-2}\}. \quad (2.15)$$

If $M=1$, then we set $r_{min}=\infty$. We say that a potential V is of *Thomas-Fermi type* if it satisfies the following two properties:

(i) There exists $\mu \geq 0$ such that for any multiindex α with $|\alpha| \leq n_0$ (where the universal constant n_0 is given in Theorem 2.2) we have

$$\left|\partial_x^\alpha \left[V(\mathbf{z}, \mathbf{r}, x) + \mu\right]\right| \leq C_\alpha f(x)^2 d(x)^{-|\alpha|}, \tag{2.16}$$

where the constants C_α depend only α, M and $\max_k z_k$;

(ii) For $|x - r_k| \leq r_{min}/2$, we have

$$-C \leq V(\mathbf{z}, \mathbf{r}, x) - \frac{z_k}{|x - r_k|} \leq C r_{min}^{-1} + C \tag{2.17}$$

where C depends on $\mathbf{z}$.

Then we have

Theorem 2.6 ([SS, Theorem 7]). *The Thomas-Fermi potential $V = V^{\mathrm{TF}}$ satisfies the conditions* (2.16) *and* (2.17). □

With these ingredients in Section 5 we will prove the following second order semiclassical asymptotics:

Theorem 2.7 (Semiclassical asymptotics with Scott term). *There exist universal constants $n_0 \in \mathbb{N}$ and $\kappa_0 > 0$ such that the following is satisfied. Let V be a real valued potential satisfying* (2.16) *and* (2.17). *Then*

$$\lim_{h\to 0} \left| \inf_A \Big(\mathrm{Tr}\, [T_h(A) - V]_- + \frac{1}{\kappa h^2} \int_{\mathbb{R}^3} |\nabla \otimes A|^2 \Big) \right. \\ \left. - 2(2\pi h)^{-3} \int_{\mathbb{R}^3\times\mathbb{R}^3} \big[p^2 - V(q)\big]_- \mathrm{d}q\mathrm{d}p - 2h^{-2} \sum_{k=1}^M z_k^2 S(z_k\kappa) \right| = 0 \tag{2.18}$$

for any $0 < \kappa \leq \kappa_0$.

Moreover, there exist some $\varepsilon > 0$ and $h_0 > 0$ and there exist an admissible vector potential A and a density matrix γ, whose density ϱ_γ satisfies

$$\int \varrho_\gamma \leq \frac{1}{3\pi^2} h^{-3} \int [V]_-^{3/2} + Ch^{-2+\varepsilon} \tag{2.19}$$

and

$$D\Big(\varrho_\gamma - (3\pi^2)^{-1} h^{-3} [V]_-^{3/2}\Big) \leq Ch^{-5+\varepsilon} \tag{2.20}$$

for any $0 < h \le h_0$, such that

$$\operatorname{Tr}\,[T_h(A) - V]\gamma + \frac{1}{\kappa h^2}\int |\nabla \otimes A|^2 \le 2(2\pi h)^{-3}\iint \big[p^2 - V(q)\big]_- \mathrm{d}q\mathrm{d}p + 2h^{-2}\sum_{k=1}^{M} z_k^2 S(z_k\kappa) + o(h^{-2}). \tag{2.21}$$

The constants C in the right hand side of these estimates depend only on κ_0, h_0 and on the constants in (2.16) *and* (2.17)*. The factor 2 in front of the semiclassical term accounts for the spin and it is present only for the Pauli case.*

Convention: All integrals, unless specified otherwise, are on $\mathbb{R}^3$.

3 Proof of the Main Theorem 1.1

In this section we complete the proof of our main theorem.

3.1 Lower bound

The first step is to reduce the many body problem to a one body problem. We will use the following Lemma whose proof relies on the Lieb-Oxford inequality [LO].

Lemma 3.1. *[ES3, Lemma 4.3] There is a universal constant $C_0 > 0$ such that for any $\Psi \in \bigwedge_1^N C_0^\infty(\mathbb{R}^3) \otimes \mathbb{C}^2$ with $\|\Psi\|_2 = 1$, for any non-negative function $\rho : \mathbb{R}^3 \to \mathbb{R}$ with $D(\rho,\rho) < \infty$, for any compactly supported and admissible A and for any $\delta > 0$ we have*

$$\Big\langle \Psi, \Big[\delta \sum_{i=1}^{N} T^{(i)}(A) + \sum_{i<j} \frac{1}{|x_i - x_j|}\Big]\Psi\Big\rangle + C_0 \int_{\mathbb{R}^3} |\nabla \times A|^2 \ge -D(\rho,\rho) + \Big\langle \Psi, \sum_{i=1}^{N} (\rho * |x_i|^{-1})\Psi \Big\rangle - C\delta^{-1}N. \quad \square$$

Thus, applying this lemma for $\varrho = \varrho_\Psi$, the density of Ψ, we get

$$\begin{aligned}
\langle \Psi, &H_N(\mathbf{Z},\mathbf{R},A)\Psi\rangle \\
&\ge \Big\langle \Psi, \sum_{j=1}^{N} \big[(1-\delta)T^{(j)}(A) - V(\mathbf{Z},\mathbf{R},x_j)\big]\Psi\Big\rangle + D(\varrho_\Psi) - C\delta^{-1}N - C_0 \int_{\mathbb{R}^3} |\nabla \times A|^2 \\
&\ge \Big\langle \Psi, \sum_{j=1}^{N} \big[(1-\delta)T^{(j)}(A) - V^{\mathrm{TF}}(\mathbf{Z},\mathbf{R},x_j)\big]\Psi\Big\rangle - D(\varrho^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}}) - C\delta^{-1}N - C_0 \int_{\mathbb{R}^3} |\nabla \times A|^2 \\
&\ge \operatorname{Tr}\,\big[(1-\delta)T(A) - V^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}}\big]_- - D(\varrho^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}}) - C\delta^{-1}N - C_0 \int_{\mathbb{R}^3} |\nabla \times A|^2,
\end{aligned}$$

where in the second step we used the definition (1.10) and that $D(\varrho_\Psi - \varrho^{\rm TF}_{\mathbf{Z},\mathbf{R}}) \geq 0$. We now add the field energy (1.5) and absorb the $-C_0 \int |\nabla \times A|^2$ term at the expense of factor $(1-\delta)$ by using

$$\frac{1}{8\pi\alpha^2} - C_0 \geq \frac{1-\delta}{8\pi\alpha^2}$$

as long as $\delta \gg Z^{-1}$ and $Z\alpha^2$ is bounded. Now we use the scaling properties (1.12) of the Thomas-Fermi theory with $h := Z^{-1/3}$ and $\kappa := 8\pi Z\alpha^2$ to get

$$\begin{aligned}
&E_{\rm abs}(\mathbf{Z},\mathbf{R},\alpha)\\
&\quad \geq Z^{7/3}\left[h^3(1-2\delta)\inf_A\Big(\mathrm{Tr}\,\big[T_h(A) - V^{\rm TF}_{\mathbf{z},\mathbf{r}}\big]_- + \frac{1}{\kappa h^2}\int |\nabla\otimes A|^2\Big) - D(\varrho^{\rm TF}_{\mathbf{z},\mathbf{r}})\right] - C\delta^{-1}N\\
&\quad\quad + \delta Z^{7/3}h^3\inf_A\Big(\mathrm{Tr}\,\big[T_h(A) - 2V^{\rm TF}_{\mathbf{z},\mathbf{r}}\big]_- + \frac{1}{\kappa h^2}\int |\nabla\otimes A|^2\Big)\\
&\quad \geq Z^{7/3}\left[\frac{2}{(2\pi)^3}\iint\Big[p^2 - V^{\rm TF}_{\mathbf{z},\mathbf{r}}(q)\Big]_-\mathrm{d}q\mathrm{d}p + 2h\sum_{k=1}^M z_k^2 S(z_k\kappa) - o(h) - D(\varrho^{\rm TF}_{\mathbf{z},\mathbf{r}})\right]\\
&\quad\quad - C\delta Z^{7/3} - C\delta^{-1}N\\
&\quad \geq Z^{7/3}\left[E^{\rm TF}_{\mathbf{z},\mathbf{r}} + 2h\sum_{k=1}^M z_k^2 S(8\pi Z_k\alpha^2) - C\delta - o(h)\right] - C\delta^{-1}N\\
&\quad \geq E^{\rm TF}_{\mathbf{Z},\mathbf{R}} + 2Z^2\sum_{k=1}^M z_k^2 S(8\pi Z_k\alpha^2) - o(Z^2) - CZ^{2-1/6}.
\end{aligned}\tag{3.1}$$

From the second to the third line we used (2.18) from Theorem 2.7 twice. In the main term the $1-2\delta$ prefactor can be easily removed for a lower bound since the term $\inf_A\big(\dots\big)$ is non-positive. In the error term we used that $\inf_A\big(\dots\big)$ is bounded by $O(h^{-3})$ since $\int [V^{\rm TF}_{\mathbf{z},\mathbf{r}}]^{5/2} \leq C$ with a constant depending only on M (see (2.16)). Then we used (1.13) and finally the scaling relation (1.12) for the energy. In the last step we also inserted the optimal $\delta = Z^{-5/6}$ and used $N = Z$. This completes the proof of the lower bound in Theorem 1.1.

3.2 Upper bound

By Lieb's variational principle [L2] and neglecting the exchange term, after a rescaling by $h = Z^{-1/3}$ the energy of the particles (1.3) can be estimated by

$$\begin{aligned}
E(\mathbf{Z},\mathbf{R},A) &\leq Z^{4/3}\Big(\mathrm{Tr}\,\big[T_h(A) - V(\mathbf{z},\mathbf{r},\cdot)\big]\gamma + ZD(Z^{-1}\varrho_\gamma)\Big)\\
&= Z^{4/3}\Big(\mathrm{Tr}\,\big[T_h(A) - V^{\rm TF}_{\mathbf{z},\mathbf{r}}\big]\gamma + ZD\big(Z^{-1}\varrho_\gamma - \varrho^{\rm TF}_{\mathbf{z},\mathbf{r}}\big) - ZD\big(\varrho^{\rm TF}_{\mathbf{z},\mathbf{r}}\big)\Big)
\end{aligned}\tag{3.2}$$

for any density matrix γ on $L^2(\mathbb{R}^3, \mathbb{C}^2)$ with density $\varrho_\gamma(x) = \mathrm{Tr}_{\mathbb{C}^2}\gamma(x,x)$ and with $\mathrm{Tr}\,\gamma = \int \varrho(x) \le N = Z$. Adding the field energy, we have

$$E_{\mathrm{abs}}(\mathbf{Z}, \mathbf{R}, \alpha) \le Z^{4/3}\Big(\mathrm{Tr}\,\big[T_h(A) - V^{\mathrm{TF}}_{\mathbf{z},\mathbf{r}}\big]\gamma + \frac{1}{8\pi Z\alpha^2}h^{-2}\int |\nabla\otimes A|^2 \\ + ZD\big(Z^{-1}\varrho_\gamma - \varrho^{\mathrm{TF}}_{\mathbf{z},\mathbf{r}}\big) - ZD\big(\varrho^{\mathrm{TF}}_{\mathbf{z},\mathbf{r}}\big)\Big) \tag{3.3}$$

for any admissible vector potential A.

Let $\kappa = 8\pi Z\alpha^2$, set $V = V^{\mathrm{TF}}_{\mathbf{z},\mathbf{r}}$ and choose an admissible vector potential A and a density matrix $\widetilde{\gamma}$ according to (2.19), (2.20) and (2.21). In particular

$$\mathrm{Tr}\,\widetilde{\gamma} = \int \varrho_{\widetilde{\gamma}} \le Z(1 + CZ^{-1/3-\varepsilon/3})$$

using that

$$\frac{1}{3\pi^2}\int [V^{\mathrm{TF}}_{\mathbf{z},\mathbf{r}}]_-^{3/2} = \int \varrho^{\mathrm{TF}}_{\mathbf{z},\mathbf{r}} = 1$$

by (1.11) and the constraint $\int \varrho = \sum_k z_k = 1$ in (1.9). We thus define $\gamma = (1+CZ^{-1/3-\varepsilon/3})^{-1}\widetilde{\gamma}$ so that the constraint $\mathrm{Tr}\,\gamma \le Z$ is satisfied. Moreover, from (2.20) we have

$$D\big(Z^{-1}\varrho_{\widetilde{\gamma}} - \varrho^{\mathrm{TF}}_{\mathbf{z},\mathbf{r}}\big) \le CZ^{-1/3-\varepsilon/3}.$$

From the triangle inequality for $\sqrt{D}$ we obtain

$$D\big(Z^{-1}\varrho_\gamma - \varrho^{\mathrm{TF}}_{\mathbf{z},\mathbf{r}}\big) \le C(1 + CZ^{-1/3-\varepsilon/3})^2 D\big(Z^{-1}\varrho_{\widetilde{\gamma}} - \varrho^{\mathrm{TF}}_{\mathbf{z},\mathbf{r}}\big) + CZ^{-2/3-2\varepsilon/3}D\big(\varrho^{\mathrm{TF}}_{\mathbf{z},\mathbf{r}}\big) \le CZ^{-1/3-\varepsilon/3}$$

using that $D\big(\varrho^{\mathrm{TF}}_{\mathbf{z},\mathbf{r}}\big) \le C$ and $\varepsilon < 1$. In summary, we obtained

$$E_{\mathrm{abs}}(\mathbf{Z}, \mathbf{R}, \alpha) \le Z^{4/3}\Big(\mathrm{Tr}\,\big[T_h(A) - V^{\mathrm{TF}}_{\mathbf{z},\mathbf{r}}\big]\gamma + \frac{1}{8\pi Z\alpha^2}h^{-2}\int |\nabla\otimes A|^2 - ZD\big(\varrho^{\mathrm{TF}}_{\mathbf{z},\mathbf{r}}\big) + CZ^{2/3-\varepsilon/3}\Big)$$

for the vector potential A from Theorem 2.7. Since (2.21) holds for $\widetilde{\gamma}$ and the energy of γ and $\widetilde{\gamma}$ differ by a factor $(1 + CZ^{-1/3-\varepsilon/3})$, we obtain, after the usual rescaling,

$$E_{\mathrm{abs}}(\mathbf{Z}, \mathbf{R}, \alpha) \\ \le Z^{7/3}\left[2(2\pi)^{-3}\iint \big[p^2 - V^{\mathrm{TF}}_{\mathbf{z},\mathbf{r}}(q)\big]_- \mathrm{d}q\mathrm{d}p - D\big(\varrho^{\mathrm{TF}}_{\mathbf{z},\mathbf{r}}\big)\right] + 2Z^2\sum_{k=1}^{M} z_k^2 S(z_k\kappa) + o(Z^2).$$

Using the identity (1.13), we thus obtain the upper bound in (1.8) which completes the proof of Theorem 1.1. □

4 The Scott term

In this section we give the proof of Theorem 2.4.

Proof of Theorem 2.4. First we prove the existence of the limit (2.12). Define, for $R > 0$ (and with κ, β as in the statement of the theorem)

$$\begin{aligned}\mathcal{E}_{R,\kappa,\beta}(A) :&= \operatorname{Tr}\Big[\phi_R\Big(T_{h=1}(A) - \frac{1}{|x|}\Big)\phi_R\Big]_- + \frac{1}{\kappa}\int_{B(R/4)} |\nabla \otimes A|^2 \\ &\quad + \beta \int_{B(2R)\setminus B(R/4)} |\nabla \otimes A|^2 - 2(2\pi)^{-3}\int_{\mathbb{R}^3\times\mathbb{R}^3} \phi_R^2(q)\Big[p^2 - \frac{1}{|q|}\Big]_- \mathrm{d}p\mathrm{d}q\end{aligned} \tag{4.1}$$

and

$$S(R,\kappa,\beta) := \frac{1}{2}\inf_A \mathcal{E}_{R,\kappa,\beta}(A). \tag{4.2}$$

We will prove later in (4.11) that this infimum is not minus infinity.

Step 1: A-priori upper bound.
Upon inserting $A = 0$ we get $S(R,\kappa,\beta) \le S(R, 0, \infty)$. Since we know that $\lim_{R\to\infty} S(R, 0, \infty) = S(0)$ exists [SSS, Lemma 4.3 with $\alpha = 0$], we obtain that $S(R,\kappa,\beta)$ is bounded from above uniformly in R. I.e., there exists a constant K_0 (independent of R, κ and β) such that

$$S(R,\kappa,\beta) \le S(R, 0, \infty) \le K_0. \tag{4.3}$$

Step 2: Lower bound and semiclassics.
Consider $r < R/8$. Let $\widetilde{\phi}_r$ satisfy $\phi_r^2 + \widetilde{\phi}_r^2 = 1$ and define $W_r = |\nabla\phi_r|^2 + |\nabla\widetilde{\phi}_r|^2$ and $\phi_{r,R} = \phi_R\widetilde{\phi}_r$. Split

$$\begin{aligned}\phi_R\Big(T_{h=1}(A) - \frac{1}{|x|}\Big)\phi_R &\ge \phi_r\Big(T_{h=1}(A) - \frac{1}{|x|}\Big)\phi_r + \phi_{r,R}\Big(T_{h=1}(A) - \frac{1}{|x|}\Big)\phi_{r,R} - W_r \\ &= \phi_r\Big(T_{h=1}(A) - \frac{1}{|x|} - W_r\Big)\phi_r + \phi_{r,R}\Big(T_{h=1}(A) - \frac{1}{|x|} - W_r\Big)\phi_{r,R}.\end{aligned} \tag{4.4}$$

The second term will be estimated by borrowing a small part of the field energy. We will use that the local semiclassical result Theorem 2.2 holds with any positive constant in front of the field energy. However, this regime has to be treated with multiscaling. The proof of the following lemma is postponed to the end of this section.

Lemma 4.1. *For any $r_0 > 0$ and $\delta > 0$ and for any r, R satisfying $r_0 \le r \le R/8$ we have*

$$\begin{aligned}\inf_A \Big\{\operatorname{Tr}\Big[\phi_{r,R}\Big(T_{h=1}(A) - \frac{1}{|x|} - W_r\Big)\phi_{r,R}\Big]_- + \delta\int_{B(2R)\setminus B(r/4)} |\nabla\otimes A|^2\Big\} \\ \ge 2(2\pi)^{-3}\int \phi_{r,R}^2(x)\Big[p^2 - \frac{1}{|x|}\Big]_- \mathrm{d}x\mathrm{d}p - C_{\delta,r_0} r^{-\varepsilon/2},\end{aligned} \tag{4.5}$$

where $\varepsilon > 0$ is the exponent obtained from Theorem 2.2 and the constant in the error term depends only on r_0 and δ.

Therefore, combining (4.4) and (4.5), we have

$$\begin{aligned}\operatorname{Tr}\Big[\phi_R\big(T_{h=1}(A) - \frac{1}{|x|}\big)\phi_R\Big]_- \geq \operatorname{Tr}\Big[\phi_r\big(T_{h=1}(A) - \frac{1}{|x|} - W_r\big)\phi_r\Big]_- \\ + 2(2\pi)^{-3}\int \phi_{r,R}^2(x)\Big[p^2 - \frac{1}{|x|}\Big]_- \mathrm{d}x\mathrm{d}p \\ - \delta\int_{B(2R)\setminus B(r/4)} |\nabla\otimes A|^2 - C_{\delta,r_0} r^{-\varepsilon/2}. \end{aligned} \tag{4.6}$$

Hence, combining the semiclassical integrals, for any $r_0 \leq r \leq R/8$ we get

$$\begin{aligned}\mathcal{E}_{R,\kappa,\beta}(A) \geq \operatorname{Tr}\Big[\phi_r\big(T_{h=1}(A) - \frac{1}{|x|} - W_r\big)\phi_r\Big]_- + \frac{1}{\kappa}\int_{B(R/4)} |\nabla\otimes A|^2 + \beta\int_{B(2R)\setminus B(R/4)} |\nabla\otimes A|^2 \\ - \delta\int_{B(2R)\setminus B(r/4)} |\nabla\otimes A|^2 \\ - 2(2\pi)^{-3}\int \phi_r^2(x)\Big[p^2 - \frac{1}{|x|}\Big]_- \mathrm{d}x\mathrm{d}p - C_{\delta,r_0} r^{-\varepsilon/2}. \end{aligned} \tag{4.7}$$

In the following, we will fix an $r_0 > 0$.

Step 3: A-priori lower bound.
We fix $r = r_0$. On the ball of radius r_0 we use that if $\kappa \leq \kappa^*$ where κ^* is a small universal constant, then

$$\operatorname{Tr}\Big[\phi_{r_0}\big(T_{h=1}(A) - \frac{1}{|x|} - W_{r_0}\big)\phi_{r_0}\Big]_- + \frac{1}{2\kappa}\int_{B(2r_0)} |\nabla\otimes A|^2 \geq -K_1 \tag{4.8}$$

and

$$-2(2\pi)^{-3}\int \phi_{r_0}^2\Big[p^2 - \frac{1}{|x|}\Big]_- \mathrm{d}x\mathrm{d}p \geq -K_2, \tag{4.9}$$

where the constants only depend on r_0. The estimate (4.9) follows by simple integration. The other estimate (4.8) is a consequence of (the proof of) [ES3, Lemma 2.1] in the case $Z = 1$.

Inserting (4.8) and (4.9) in (4.7), we get

$$\mathcal{E}_{R,\kappa,\beta}(A) \geq \big(\frac{1}{2\kappa} - \delta\big)\int_{B(R/2)} |\nabla\otimes A|^2 + (\beta - \delta)\int_{B(2R)\setminus B(R/2)} |\nabla\otimes A|^2 - K(r_0,\delta) \tag{4.10}$$

for any $\kappa \leq \kappa^*$ and with a finite constant $K(r_0,\delta)$ depending only on r_0 and δ. Choosing $\delta = \beta \leq (2\kappa)^{-1}$, this proves in particular that

$$S(R,\kappa,\beta) > -\infty, \tag{4.11}$$

and with the choice $\delta = (2\kappa^*)^{-1}$ we get

$$S(R, \kappa, (2\kappa)^{-1}) \geq -C(\kappa^*) \tag{4.12}$$

for some finite function $C(\kappa^*) < \infty$ depending only on r_0 and κ^* as long as $\kappa \leq \kappa^*$.

Step 4: Bound on the magnetic energy.

From (4.10) we also obtain that if A is such that it yields a better energy on the large ball than no-magnetic field, i.e.

$$\mathcal{E}_{R,\kappa,\beta}(A) \leq \mathcal{E}_{R,\kappa,\beta}(A = 0),$$

and $\kappa \leq \kappa^*$, then

$$\int_{B(2R)} |\nabla \otimes A|^2 \leq C(r_0, \beta) \tag{4.13}$$

with some constant depending only on r_0 and β. This follows from (4.10) (taking $\delta = \delta_0(\beta) := \frac{1}{2}\min((2\kappa^*)^{-1}, \beta))$ because then we have

$$\frac{\delta_0(\beta)}{2} \int_{B(2R)} |\nabla \otimes A|^2 \leq \mathcal{E}_{R,\kappa,\beta}(A = 0) + K(r_0, \delta_0(\beta)),$$

and $\mathcal{E}_{R,\kappa,\beta}(A = 0)$ is known to have a finite limit as $R \to \infty$, independent of κ, β [SSS, Lemma 4.3].

Step 5: Bound on the localization error.

We will now remove the localisation error W_r from (4.7) using the bound on the field energy. By the variational principle and $W_r \leq Cr^{-2}$, we can estimate

$$\begin{aligned} \mathrm{Tr}\,\Big[\phi_r\big(T_{h=1}(A) - \frac{1}{|x|} - W_r\big)\phi_r\Big]_- &\geq \mathrm{Tr}\,\Big[\phi_r\big(T_{h=1}(A) - \frac{1}{|x|}\big)\phi_r\Big]_- \\ &\quad - Cr^{-2}\mathrm{Tr}\,\mathbf{1}_{(-\infty,0)}\Big(\phi_r\big(T_{h=1}(A) - \frac{1}{|x|} - W_r\big)\phi_r\Big). \end{aligned} \tag{4.14}$$

We have, with $g_r = \mathbf{1}_{\{|x|\leq r\}}$,

$$\begin{aligned} \mathrm{Tr}\,\mathbf{1}_{(-\infty,0)}\Big(\phi_r\big(T_{h=1}(A) - \frac{1}{|x|} - W_r\big)\phi_r\Big) &\leq \mathrm{Tr}\,\mathbf{1}_{(-\infty,0)}\Big(\phi_r\Big[(p+A)^2 - \frac{1}{|x|} - |B| - Cr^{-2}\Big]\phi_r\Big) \\ &\leq \mathrm{Tr}\,\mathbf{1}_{(-\infty,0)}\Big((p+A)^2 - \Big[\frac{1}{|x|} + |B| + Cr^{-2}\Big]g_r\Big). \end{aligned}$$

Here we used the fact that we consider the strictly negative eigenvalues to get the last inequality. By the CLR estimate, we therefore have

$$\begin{aligned} \mathrm{Tr}\,\mathbf{1}_{(-\infty,0)}\Big(\phi_r\big(T_{h=1}(A) - \frac{1}{|x|} - W_r\big)\phi_r\Big) &\leq C\int_{\{|x|\leq r\}} \Big[\frac{1}{|x|} + |B| + Cr^{-2}\Big]^{3/2}\mathrm{d}x \\ &\leq C'\int_{\{|x|\leq r\}} \Big[\frac{1}{|x|^{3/2}} + |B|^{3/2} + Cr^{-3}\Big]\mathrm{d}x \\ &\leq C''\Big\{r^{3/2} + r^{3/4}\Big(\int_{\{|x|\leq r\}} |B|^2\Big)^{3/4}\Big\}, \end{aligned}$$

where we used the Hölder inequality to get the last inequality. Using the uniform bound (4.13) on the field energy, we can therefore control the last term in (4.14) for any $r \geq r_0$ as

$$r^{-2}\mathrm{Tr}\ \mathbf{1}_{(-\infty,0)}\Big(\phi_r\big(T_{h=1}(A) - \frac{1}{|x|} - W_r\big)\phi_r\Big) \leq C_{r_0} r^{-1/2}. \tag{4.15}$$

Thus

$$\mathrm{Tr}\ \Big[\phi_r\big(T_{h=1}(A) - \frac{1}{|x|} - W_r\big)\phi_r\Big]_- \geq \mathrm{Tr}\ \Big[\phi_r\big(T_{h=1}(A) - \frac{1}{|x|}\big)\phi_r\Big]_- - C_{r_0} r^{-1/2}. \tag{4.16}$$

Step 6: Monotonicity of the energy in the radius.

Combining (4.7), (4.16) and the definition (4.1) with R replaced with r and β replaced with β' we get

$$\begin{aligned}\mathcal{E}_{R,\kappa,\beta}(A) &\geq \mathcal{E}_{r,\kappa,\beta'}(A) - C_{\delta,r_0} r^{-\varepsilon/2}\\ &\quad + \left[\frac{1}{\kappa}\int_{B(R/4)\setminus B(r/4)} + \beta\int_{B(2R)\setminus B(R/4)} - \beta'\int_{B(2r)\setminus B(r/4)} - \delta\int_{B(2R)\setminus B(r/4)}\right]|\nabla\otimes A|^2\\ &\geq \mathcal{E}_{r,\kappa,\beta'}(A) + \frac{\beta}{2}\int_{B(2R)\setminus B(r/4)}|\nabla\otimes A|^2 - C_{\delta_0,r_0} r^{-\varepsilon/2}\end{aligned} \tag{4.17}$$

for any $\beta', \beta \leq 1/(2\kappa)$ and if we choose $\delta = \delta_0(\kappa,\beta) := \frac{1}{2}\min\{(2\kappa)^{-1}, \beta\}$ and recall that $r \leq R/8$. Notice that we even saved a part of the field energy in $B(2R) \setminus B(r/4)$. Taking infimum over all A, we have

$$S(R,\kappa,\beta) \geq S(r,\kappa,\beta') - C_{\delta_0,r_0} r^{-\varepsilon/2} \tag{4.18}$$

which shows that $R \to S(R,\kappa,\beta)$ is essentially an increasing function with a uniform upper bound (4.3), hence it has a limit. To be more precise, define $S(\kappa,\beta) := \limsup_{R\to\infty} S(R,\kappa,\beta)$, then for any $\eta > 0$ there is a sufficiently large $r = r(\eta) > r_0$ such that $C_{\delta_0,r_0} r^{-\varepsilon/2} \leq \eta/2$ and $S(r,\kappa,\beta) \geq S(\kappa,\beta) - \eta/2$. Then (4.18) implies that $S(R,\kappa,\beta) \geq S(\kappa,\beta) - \eta$ for any $R \geq 8r(\eta)$. Together with the definition of $S(\kappa,\beta)$ this means that $S(\kappa,\beta) = \lim_{R\to\infty} S(R,\kappa,\beta)$.

Step 7: Independence of the limit of β.

Suppose that $\beta < \beta' \leq 1/(2\kappa)$. Then clearly $S(R,\kappa,\beta) \leq S(R,\kappa,\beta')$. Furthermore, by taking first the limit $R \to \infty$ in (4.18), then the limit $r \to \infty$ we obtain that

$$\lim_{R\to\infty} S(R,\kappa,\beta) \geq \lim_{R\to\infty} S(R,\kappa,\beta').$$

So we get that the limit $S(\kappa,\beta)$ is indeed independent of $\beta \leq 1/(2\kappa)$. Moreover, from (4.18) it follows that

$$S(\kappa) \geq S(r,\kappa,\beta) - C_{\delta_0,r_0} r^{-\varepsilon/2} \tag{4.19}$$

for any $r \geq r_0$, $\beta \leq 1/(2\kappa)$ and $\delta_0(\kappa, \beta) := \frac{1}{2}\min\{(2\kappa)^{-1}, \beta\}$. Combining this bound with (4.12), we obtain in particular that

$$\inf_{\kappa \leq \kappa^*} S(\kappa) \geq C(\kappa^*, r_0) > -\infty \tag{4.20}$$

for some constant depending only on κ^* and r_0. Together with the upper bound (4.3) this shows that $S(\kappa)$ is a bounded function for $\kappa \in (0, \kappa^*]$.

The fact that $S(0) = \frac{1}{8}$, i.e. the non-magnetic case, has been proven before, see e.g. Lemma 4.3 in [SSS] with the choice $\alpha = 0$. (Note that in [SSS] $S(0) = \frac{1}{4}$ is stated but there the kinetic energy was $-\frac{1}{2}\Delta$, while our non-magnetic kinetic energy is $-\Delta$ which accounts for the apparent discrepancy.)

It remains to prove that one can obtain $S(\kappa)$ by considering only vector potentials with small support.

Step 8: Improved bound on field energy.
Let A_R be an (almost) minimizer of the variational problem (4.2), i.e.

$$2S(R, \kappa, \beta) \geq \mathcal{E}_{R,\kappa,\beta}(A_R) - R^{-\varepsilon/2}.$$

Using (4.17) with the choice $r = R/8$, $\beta' = \beta$ and estimating $\mathcal{E}_{R/8,\kappa,\beta}(A_R) \geq 2S(R/8, \kappa, \beta)$, we get

$$S(R, \kappa, \beta) \geq S(R/8, \kappa, \beta) + \frac{\beta}{2}\int_{B(2R)\setminus B(R/32)} |\nabla \otimes A_R|^2 - C_{\delta_0, r_0} R^{-\varepsilon/2} \tag{4.21}$$

for any $R \geq 8r_0$. Now letting $R \to \infty$, we conclude that

$$\lim_{R\to\infty} \frac{\beta}{2}\int_{B(2R)\setminus B(R/32)} |\nabla \otimes A_R|^2 = 0. \tag{4.22}$$

Step 9: Upper bound on $S(R, \kappa, \beta)$.
Fix $r = R/8$ and κ, β. By the definition of $S(r, \kappa, \beta)$, there exists a vector potential A_r such that

$$2S(r, \kappa, \beta) \geq \mathcal{E}_{r,\kappa,\beta}(A_r) - r^{-1}, \tag{4.23}$$

and we can assume that

$$\int_{B(2r)\setminus B(r/4)} A_r = 0 \tag{4.24}$$

by adding a constant to A_r if necessary. Finally, by (4.22) we have

$$e(r) := \int_{B(2r)\setminus B(r/32)} |\nabla \otimes A_r|^2 = o(1), \tag{4.25}$$

as $r \to \infty$.

Furthermore, there exists a density matrix γ_r such that

$$2S(r,\kappa,\beta) \geq \mathrm{Tr}\ \phi_r\gamma_r\phi_r\Big(T_{h=1}(A_r) - \frac{1}{|x|}\Big) + \frac{1}{\kappa}\int_{B(r/4)} |\nabla\otimes A_r|^2 \tag{4.26}$$
$$+ \beta\int_{B(2r)\setminus B(r/4)} |\nabla\otimes A_r|^2 - 2(2\pi)^{-3}\int_{\mathbb{R}^3\times\mathbb{R}^3} \phi_r^2(q)\Big[p^2 - \frac{1}{|q|}\Big]_- \mathrm{d}p\mathrm{d}q - 2r^{-1}.$$

We define $A_r' := \phi_{2r}A_r$, then $A_r' = A_r$ on the support of ϕ_r. Moreover,

$$\int_{B(2r)\setminus B(r/4)} |\nabla\otimes A_r'|^2 \leq Cr^{-2}\int_{B(2r)\setminus B(r/4)} |A_r|^2 + \int_{B(2r)\setminus B(r/4)} \phi_{2r}^2|\nabla\otimes A_r|^2$$
$$\leq C\int_{B(2r)\setminus B(r/4)} |\nabla\otimes A_r|^2 \leq Ce(r) \tag{4.27}$$

with a universal constant C. Here we used the Poincaré inequality on the ring $B(2r)\setminus B(r/4)$ which holds with a universal constant since the width of the ring is comparable with its radius.

Thus, we have from (4.26)

$$2S(r,\kappa,\beta) \geq \mathrm{Tr}\ \phi_r\gamma_r\phi_r\Big(T_{h=1}(A_r') - \frac{1}{|x|}\Big) + \frac{1}{\kappa}\int_{B(r/4)} |\nabla\otimes A_r'|^2 \tag{4.28}$$
$$- 2(2\pi)^{-3}\int_{\mathbb{R}^3\times\mathbb{R}^3} \phi_r^2(q)\Big[p^2 - \frac{1}{|q|}\Big]_- \mathrm{d}p\mathrm{d}q - C(r^{-1} + e(r)).$$

We use this A_r' as a trial vector potential for $S(R,\kappa,\beta)$, i.e. we have

$$2S(R,\kappa,\beta) \leq \mathrm{Tr}\ \Big[\phi_R\Big(T_{h=1}(A_r') - \frac{1}{|x|}\Big)\phi_R\Big]_- + \frac{1}{\kappa}\int_{B(2r)} |\nabla\otimes A_r'|^2 \tag{4.29}$$
$$- 2(2\pi)^{-3}\int_{\mathbb{R}^3\times\mathbb{R}^3} \phi_R^2(q)\Big[p^2 - \frac{1}{|q|}\Big]_- \mathrm{d}p\mathrm{d}q.$$

The field energy integral (with coefficient κ^{-1} in (4.1)) can be restricted to $B(2r)$ and the second field energy integral is absent since A_r' is supported on $B(2r)$.

Now we construct a suitable trial density matrix γ. It will have the form

$$\gamma := \phi_r\gamma_r\phi_r + \phi_{r,R}\widetilde{\gamma}\phi_{r,R},$$

with $0 \leq \widetilde{\gamma} \leq 1$ to be chosen below. Inserting γ into (4.29) and using the support properties of the cutoff functions, we obtain

$$\begin{aligned}2S(R,\kappa,\beta) \leq& \mathcal{E}_{R,\kappa,\beta}(A_r')\\ \leq& \mathrm{Tr}\ \phi_r\gamma_r\phi_r\Big(T_{h=1}(A_r') - \frac{1}{|x|}\Big) + \mathrm{Tr}\ \phi_{r,R}\widetilde{\gamma}\phi_{r,R}\Big(T_{h=1}(A_r') - \frac{1}{|x|}\Big)\\ &+ \frac{1}{\kappa}\int_{B(2r)} |\nabla\otimes A_r'|^2 - 2(2\pi)^{-3}\int_{\mathbb{R}^3\times\mathbb{R}^3} \phi_R^2(q)\Big[p^2 - \frac{1}{|q|}\Big]_- \mathrm{d}p\mathrm{d}q\\ \leq& 2S(r,\kappa,\beta) + C(e(r) + r^{-1}) + \Delta(\widetilde{\gamma}),\end{aligned} \tag{4.30}$$

where

$$\Delta(\widetilde{\gamma}) := \mathrm{Tr}\ \phi_{r,R}\widetilde{\gamma}\phi_{r,R}\Big(T_{h=1}(A_r') - \frac{1}{|x|}\Big) - 2(2\pi)^{-3}\int_{\mathbb{R}^3\times\mathbb{R}^3}\phi_{r,R}^2(q)\Big[p^2 - \frac{1}{|q|}\Big]_- \mathrm{d}p\mathrm{d}q. \tag{4.31}$$

We used (4.23), (4.26) and (4.27) in the last step of (4.30).

We will use Theorem 2.3 and multiscaling to prove that we may choose $\widetilde{\gamma}$ such that

$$\Delta(\widetilde{\gamma}) \le C(\sqrt{e(r)} + r^{-1/2}). \tag{4.32}$$

Inserting (4.32) in (4.30) and recalling that $e(r)\to 0$ by (4.25) we obtain (2.13) (with the choice $A_R = A_r'$). Here we used the choice that $r = R/8$ and the previous result that $S(\kappa) = \lim_{R\to\infty} S(R,\kappa,\beta)$ exists and is independent of β.

It thus remains to prove (4.32) for a suitable choice of $\widetilde{\gamma}$. Let ψ_u be given as in Lemma 2.1 with the choice $\ell(u) = \ell_u := \frac{1}{100}\sqrt{r_0^2+u^2}$. Define

$$\widetilde{\gamma} := \int_{\mathcal{P}} \psi_u\gamma_u\psi_u \frac{\mathrm{d}u}{\ell_u^3},$$

where

$$\mathcal{P} := \{x\ :\ r/3 < |x| < R\}$$

and

$$\gamma_u = \mathbf{1}_{(-\infty,0]}\Big[\psi_u\phi_{r,R}\Big(T_{h=1}(A_r') - \frac{1}{|x|}\Big)\phi_{r,R}\psi_u\Big].$$

Clearly $0\le\widetilde{\gamma}\le 1$ using (2.2).

Inserting this choice of $\widetilde{\gamma}$ into (4.29) and using (2.2), we obtain

$$\begin{aligned}\Delta(\widetilde{\gamma}) = \int_{\mathcal{P}}\frac{\mathrm{d}u}{\ell_u^3}\Big\{&\mathrm{Tr}\ \Big[\phi_{r,R}\psi_u\Big(T_{h=1}(A_r') - \frac{1}{|x|}\Big)\psi_u\phi_{r,R}\Big]_- \\ &- 2(2\pi)^{-3}\int_{\mathbb{R}^3\times\mathbb{R}^3}\phi_{r,R}^2(q)\psi_u^2(q)\Big[p^2 - \frac{1}{|q|}\Big]_-\mathrm{d}p\mathrm{d}q\Big\}.\end{aligned} \tag{4.33}$$

Notice that we could restrict the du integration to $\mathcal{P}$ since otherwise $\psi_u\phi_{r,R}$ vanishes due to the support properties of these functions.

We will use Theorem 2.3 for each u with

$$h = 1, \qquad f_u^{-2} = \ell_u.$$

We have

$$h^2 f_u^{-4}\ell_u^{-3}\int_{B(u,2\ell_u)}|\nabla\otimes A_r'|^2 \le \ell_u^{-1}\int_{B(2R)\setminus B(r/4)}|\nabla\otimes A_r'|^2 \le Ce(r),$$

by (4.27). Here we used that supp $A_r'\subseteq B(2r)$ to get the last inequality. So (2.10) is satisfied and we get from (2.11) and (4.33) that

$$\Delta(\widetilde{\gamma}) \le C\int_{\mathcal{P}}\frac{\mathrm{d}u}{\ell_u^3}\Big\{e(r)^{1/2} + \ell_u^{-1/2}\Big\} \le C\Big(e(r)^{1/2} + r^{-1/2}\Big) \tag{4.34}$$

for $r\ge r_0$. This finishes the proof of (4.32). □

Proof of Lemma 4.1. We choose $\ell(u) = \ell_u := \frac{1}{100}\sqrt{r_0^2 + u^2}$ and $f_u = \ell_u^{-1/2}$ for the scaling functions and define the ring

$$\mathcal{P} := \{x \ : \ r/3 < |x| < R\}$$

which supports $\phi_{r,R}$. Inserting the partition of unity (2.2) and reallocating the localization error we get

$$\begin{aligned}
&\mathrm{Tr}\,\Big[\phi_{r,R}\big(T_1(A) - \frac{1}{|x|} - W_r\big)\phi_{r,R}\Big]_- \\
&\qquad = \mathrm{Tr}\,\Big[\int_{\mathcal{P}} \frac{\mathrm{d}u}{\ell_u^3}\Big(\psi_u\phi_{r,R}\big(T_1(A) - \frac{1}{|x|} - W_r\big)\phi_{r,R}\psi_u - |\nabla\psi_u|^2\phi_{r,R}^2\Big)\Big]_- \\
&\qquad \geq \int_{\mathcal{P}} \frac{\mathrm{d}u}{\ell_u^3}\mathrm{Tr}\,\Big[\psi_u\phi_{r,R}\Big(T_1(A) - \frac{1}{|x|} - C\big(W_r + |\nabla\psi_u|^2\big)\Big)\phi_{r,R}\psi_u\Big]_- .
\end{aligned}$$

Notice that we could restrict the $\mathrm{d}u$ integration to $\mathcal{P}$ since otherwise $\psi_u\phi_{r,R}$ vanishes due to the support properties of these functions. We also used that $\mathrm{Tr}\,[\int O_u \mathrm{d}\mu(u)]_- \geq \int \mathrm{Tr}\,[O_u]_- \mathrm{d}\mu(u)$ for any continuous family of operators O_u and for any measure μ. We can also reallocate the field energy as

$$\int_{B(2R)\setminus B(r/4)} |\nabla\otimes A|^2 \geq c\int_{\mathcal{P}} \frac{\mathrm{d}u}{\ell_u^3}\int_{B_u(2\ell_u)} |\nabla\otimes A|^2$$

with some positive universal constant c. Thus

$$\mathrm{Tr}\,\Big[\phi_{r,R}\big(T_1(A) - \frac{1}{|x|} - W_r\big)\phi_{r,R}\Big]_- + \delta\int_{B(2R)\setminus B(r/4)} |\nabla\otimes A|^2 \geq \int_{\mathcal{P}} \frac{\mathrm{d}u}{\ell_u^3}\mathcal{E}_{r,R}(A, V^+, \psi_u), \quad (4.35)$$

where we define

$$\mathcal{E}_{r,R}(A, U, \psi_u) := \mathrm{Tr}\,\Big[\psi_u\phi_{r,R}\big(T_1(A) - U\big)\phi_{r,R}\psi_u\Big]_- + c\int_{B_u(2\ell_u)} |\nabla\otimes A|^2$$

for any potential U, and in the last step we used that

$$\frac{1}{|x|} + C\big(W_r + |\nabla\psi_u|^2\big) \leq \frac{1}{|x|}\Big(1 + \frac{C}{r}\Big) =: V^+(x).$$

This inequality holds for any $u \in \mathcal{P}$ by the support and scaling properties of W_r and ψ_u and by the estimate $W_r \leq Cr^{-2}\mathbf{1}(r/2 \leq |x| \leq r) \leq Cr^{-1}/|x|$.

It is easy to see that $\psi = \psi_u\phi_{r,R}$ and $V = V^+$ satisfy the condition (2.7) in Theorem 2.2 on the ball $B_u(2\ell_u)$ (the theorem was formulated for balls about the origin but it clearly holds for balls with different center). We can choose $h_0 \geq 1$ and κ_0 sufficiently large so that $c\delta \geq \kappa_0^{-1}$ and $1 \leq h_0 f_u \ell_u = \frac{1}{10}h_0(1 + u^2)^{1/4}$ are satisfied for all $u \in \mathcal{P}$ and $r \geq r_0$. Thus, Theorem 2.2 with $h = 1$ gives

$$\mathcal{E}_{r,R}(A, V^+, \psi_u) \geq 2(2\pi)^{-3}\iint [(\psi_u\phi_{r,R})(x)]^2[p^2 - V^+(x)]_- \mathrm{d}x\mathrm{d}p - C_{\delta,r_0}\ell_u^{-\varepsilon/2},$$

where the constant C_{δ,r_0} is independent of u but it depends on δ and on r_0 (via the choice of κ_0 and h_0).

Inserting this bound into (4.35), we get

$$\begin{aligned}\mathrm{Tr}\,\Big[\phi_{r,R}\big(T_1(A) - \frac{1}{|x|} - W_r\big)\phi_{r,R}\Big]_- + \delta \int_{B(2R)\setminus B(r/4)} |\nabla\otimes A|^2 \\ \geq 2(2\pi)^{-3} \iint \phi_{r,R}(x)^2 [p^2 - V^+(x)]_- \mathrm{d}x\mathrm{d}p - C_{\delta,r_0}\int_{\mathcal{P}} \frac{\mathrm{d}u}{\ell_u^{3+\varepsilon/2}},\end{aligned}$$

where in the first term we extended the $\mathrm{d}u$ integration from $\mathcal{P}$ to $\mathbb{R}^3$ and we used (2.2). The last integral is bounded by $C_{\delta,r_0} r^{-\varepsilon/2}$, uniformly in R.

Finally, we can remove the localization errors from V^+, since

$$\begin{aligned}\iint \phi_{r,R}(x)^2 \Big([p^2 - V^+(x)]_- - [p^2 - |x|^{-1}]_-\Big)\mathrm{d}x\mathrm{d}p \\ \leq C \int_{|x|\geq r/2} \frac{1}{|x|^{5/2}}\Big[\Big(1+\frac{C}{r}\Big)^{5/2} - 1\Big]\mathrm{d}x \\ \leq C r^{-1/2} \end{aligned} \tag{4.36}$$

with a constant independent of R. This error can be absorbed into the other error as $\varepsilon \leq 1$. Thus we get (4.5) and have proved Lemma 4.1. □

5 Semiclassics with Scott term

In this section we prove Theorem 2.7. The guiding principle follows the similar proofs in [SS, SSS]. We first divide the space into three regions. The first region consists of disjoint balls of radius $r \sim h$ about the nuclei. Here we will use the Scott asymptotics as described in Theorem 2.4. The second region is far away from the nuclei, at a distance $R \gtrsim h^{-1}$. The contribution of this regime will be estimated by a simple Lieb-Thirring inequality. Finally, in the third intermediate region, we will use an argument similar to Lemma 4.1 which relied on the multiscale decomposition and Theorem 2.2 on each domain. The precise decomposition is the following.

Choose two localization functions $\theta_\pm \in C^1(\mathbb{R})$ with the properties that $0 \leq \theta_\pm \leq 1$, $\theta_-^2 + \theta_+^2 \equiv 1$, moreover $\theta_-(t) = 1$ for $t < 1/2$ and $\theta_-(t) = 0$ for $t \geq 1$. Recall that $d(x)$ denotes the distance of x to the nearest nucleus and r_{min} is the minimal distance among the nuclei.

For any $r < r_{min}/4$ and $R > r_{min}$ we set

$$\phi_\pm(x) := \theta_\pm\Big(\frac{d(x)}{r}\Big), \qquad \Phi_\pm(x) := \theta_\pm\Big(\frac{d(x)}{R}\Big).$$

Note that

$$\phi_-(x) = \sum_{k=1}^{M} \theta_{r,k}(x), \qquad \text{with} \quad \theta_{r,k}(x) = \theta_-(|x - r_k|/r).$$

Assuming h is small enough, we will choose

$$r := h^{1-\xi}, \qquad R := \begin{cases} Ch^{-1/2} & \text{if } \mu = 0 \\ CR_\mu & \text{if } \mu \neq 0 \end{cases} \tag{5.1}$$

with some small $\xi > 0$. Here the μ-dependent constant $R_\mu > 0$ is chosen such that $-V(x) \geq 0$ for $d(x) \geq R_\mu/2$. Clearly $\Phi_-^2 + \Phi_+^2 = 1$, $\phi_-^2 + \phi_+^2 = 1$ and

$$\phi_-^2 + \Phi_+^2 + \Phi_-^2\phi_+^2 = 1.$$

This latter partition of unity corresponds to the three regions we described above. The localization errors will be affordable in all regimes. Near the nuclei, the localization errors of order $h^2r^{-2} = O(h^{2\xi})$ is more than one order of magnitude smaller than the size of the potential in this regime, which is $|x - r_k|^{-1} \sim h^{-1}$, and the localization error relative to the potential becomes even weaker further away from the nuclei. The localization error far away is of order $h^2R^{-2} = h^3$ will be negligible both in $L^{5/2}$ and L^4 norms as necessary for the magnetic Lieb-Thirring inequality that we recall for convenience:

Theorem 5.1. *[LLS] There exist a universal constant C such that for the semiclassical Pauli operator $T_h(A) - V$ with a potential $V \in L^{5/2}(\mathbb{R}^3) \cap L^4(\mathbb{R}^3)$ and magnetic field $B = \nabla \times A \in L^2(\mathbb{R}^3)$ we have*

$$\mathrm{Tr}\,\big[T_h(A) - V\big]_- \leq Ch^{-3}\int [V]_+^{5/2} + C\Big(h^{-2}\int |B|^2\Big)^{3/4}\Big(\int [V]_+^4\Big)^{1/4}. \tag{5.2}$$

5.1 Lower bound

For any $\varepsilon \in (0, 1/4)$, we define

$$\begin{aligned} \mathcal{T}_k(A) :&= \mathrm{Tr}\,\Big[\theta_{r,k}\big(T_h(A) - V - Ch^2r^{-2}\big)\theta_{r,k}\Big]_- + \Big(1 - \frac{\varepsilon}{2}\Big)\frac{1}{\kappa h^2}\int_{B_{r_k}(r/4)} |\nabla \otimes A|^2 \\ &\quad + \frac{1}{4\kappa h^2}\int_{B_{r_k}(2r)\setminus B_{r_k}(r/4)} |\nabla \otimes A|^2. \end{aligned} \tag{5.3}$$

Using the IMS localization and the fact that the balls $B_{r_k}(2r)$ are disjoint since $r < r_{min}/4$, we have

$$\begin{aligned} &\mathrm{Tr}\,[T_h(A) - V]_- + \frac{1}{\kappa h^2}\int_{\mathbb{R}^3} |\nabla \otimes A|^2 \\ &\qquad \geq \sum_{k=1}^{M} \mathcal{T}_k(A) \\ &\qquad + \mathrm{Tr}\,\Big[\Phi_+\big(T_h(A) - V - Ch^2W_R\big)\Phi_+\Big]_- + \frac{\varepsilon}{2\kappa h^2}\int_{\mathbb{R}^3} |\nabla \otimes A|^2 \\ &\qquad + \mathrm{Tr}\,\Big[\Phi_-\phi_+\big(T_h(A) - V - Ch^2W_{r,R}\big)\phi_+\Phi_-\Big]_- + \frac{1}{8\kappa h^2}\int_{\mathbb{R}^3\setminus\bigcup_k B_{r_k}(r/4)} |\nabla \otimes A|^2 \end{aligned} \tag{5.4}$$

with some positive universal constant C and with $W_R := |\nabla\Phi_-|^2 + |\nabla\Phi_+|^2$ and $W_{r,R} := |\nabla\phi_-|^2 + |\nabla\phi_+|^2 + |\nabla\Phi_-|^2 + |\nabla\Phi_+|^2$.

First line in (5.4)

Fix k and recall from (2.17) that

$$-V(x) \geq -\frac{z_k}{|x-r_k|} - Cr_{min}^{-1} - C$$

on the support of $\theta_{r,k}$. Thus we can write

$$\mathcal{T}_k(A) \geq \mathcal{T}_k^{(1)}(A) + \mathcal{T}_k^{(2)}(A) + \mathcal{T}_k^{(3)}(A),$$

where

$$\begin{aligned}
\mathcal{T}_k^{(1)}(A) :=& \mathrm{Tr}\left[\theta_{r,k}\big((1-2\varepsilon)T_h(A) - (1-2\varepsilon)\frac{z_k}{|x-r_k|}\big)\theta_{r,k}\right]_- \\
&+ \frac{1-2\varepsilon}{\kappa h^2}\int_{B_{r_k}(2r)} |\nabla\otimes A|^2 + \frac{1-2\varepsilon}{8\kappa h^2}\int_{B_{r_k}(2r)\setminus B_{r_k}(r/4)} |\nabla\otimes A|^2 \\
\mathcal{T}_k^{(2)}(A) :=& \mathrm{Tr}\left[\theta_{r,k}\big(\varepsilon T_h(A) - Ch^2r^{-2} - Cr_{min}^{-1} - C\big)\theta_{r,k}\right]_- + \frac{\varepsilon}{4\kappa h^2}\int_{B_{r_k}(2r)} |\nabla\otimes A|^2. \\
\mathcal{T}_k^{(3)}(A) :=& \mathrm{Tr}\left[\theta_{r,k}\big(\varepsilon T_h(A) - 2\varepsilon\frac{z_k}{|x-r_k|}\big)\theta_{r,k}\right]_- + \frac{\varepsilon}{4\kappa h^2}\int_{B_{r_k}(2r)} |\nabla\otimes A|^2.
\end{aligned}$$

After pulling out the common $(1-2\varepsilon)$ factor, shifting r_k to the origin and rescaling, we obtain from (2.12), with $\beta = (8\kappa)^{-1}$, that

$$\inf_A \mathcal{T}_k^{(1)}(A) \geq (1-2\varepsilon)\left[2(2\pi h)^{-3}\int_{\mathbb{R}^3\times\mathbb{R}^3} \theta_{r,k}^2\left[p^2 - \frac{z_k}{|q-r_k|}\right]_- \mathrm{d}q\mathrm{d}p + 2h^{-2}z_k^2 S(z_k\kappa)\right] + o(h^{-2}).$$

Here we made use of the fact that after rescaling the variable R in (2.12) becomes $rh^{-1} = h^{-\xi}$, so the limit $h \to 0$ is equivalent to the limit $R \to \infty$ in (2.12).

The term in the square bracket can be bounded by

$$\begin{aligned}
&\left|2(2\pi h)^{-3}\int_{\mathbb{R}^3\times\mathbb{R}^3} \theta_{r,k}^2\left[p^2 - \frac{z_k}{|q-r_k|}\right]_- \mathrm{d}q\mathrm{d}p + 2h^{-2}z_k^2 S(z_k\kappa)\right| \\
&\qquad \leq Ch^{-3}\int_{|q-r_k|\leq r} \frac{\mathrm{d}q}{|q-r_k|^{5/2}} + Ch^{-2} \\
&\qquad \leq Ch^{-3}r^{1/2} + Ch^{-2},
\end{aligned} \tag{5.5}$$

using $z_k \leq 1$ and S is bounded (if $\kappa \leq \kappa_0$ is sufficiently small). Thus

$$\inf_A \mathcal{T}_k^{(1)}(A) \geq \left[2(2\pi h)^{-3}\int_{\mathbb{R}^3\times\mathbb{R}^3} \theta_{r,k}^2\left[p^2 - \frac{z_k}{|q-r_k|}\right]_- \mathrm{d}q\mathrm{d}p + 2h^{-2}z_k^2 S(z_k\kappa)\right] + o(h^{-2})$$

as long as $\varepsilon r^{1/2} \ll h$.

The term $\mathcal{T}_k^{(2)}(A)$ is estimated by the magnetic Lieb-Thirring inequality (5.2) which we need in the following form:

Lemma 5.2. *Let $\phi \in C_0^\infty(\mathbb{R}^3)$ be a cutoff function with supp $\phi \subset B(1)$, $\phi \equiv 1$ on $B(1/2)$. Define $\phi_\ell(x) = \phi(x/\ell)$ for some $\ell > 0$ and let $\Omega := supp\, \phi_\ell$. Then for any vector potential A we have*

$$\mathrm{Tr}\,\big[\phi_\ell(T_h(A) - V)\phi_\ell\big]_- + \frac{\beta}{h^2}\int_{B(2\ell)} |\nabla \otimes A|^2 \geq -Ch^{-3}\int_\Omega V_+^{5/2} - C\beta^{-3}\int_\Omega V_+^4 \tag{5.6}$$

with some universal constant C.

Proof. Let $\widetilde{\phi}_\ell(x) := \widetilde{\phi}(x/\ell)$, where $\widetilde{\phi} \in C_0^\infty(\mathbb{R}^3)$ is supported in $B(3/2)$ and $\widetilde{\phi} \equiv 1$ on $B(1)$. Set $\langle A\rangle := |B(2\ell)|^{-1}\int_{B(2\ell)} A$ and $\widetilde{A} := (A - \langle A\rangle)\widetilde{\phi}_\ell$. By a gauge transformation and by the fact that $\widetilde{A} = A - \langle A\rangle$ on the support of ϕ_ℓ, we have

$$\mathrm{Tr}\,\big[\phi_\ell(T_h(A) - V)\phi_\ell\big]_- = \mathrm{Tr}\,\big[\phi_\ell(T_h(\widetilde{A}) - V)\phi_\ell\big]_-.$$

By the magnetic Lieb-Thirring inequality (5.2) we have

$$\mathrm{Tr}\,\big[\phi_\ell(T_h(\widetilde{A}) - V)\phi_\ell\big]_- \geq -Ch^{-3}\int_\Omega V_+^{5/2} - C\Big(h^{-2}\int_{\mathbb{R}^3}|\nabla\times\widetilde{A}|^2\Big)^{3/4}\Big(\int_\Omega V_+^4\Big)^{1/4}. \tag{5.7}$$

By supp $\widetilde{A} \subset B(2\ell)$ and by the Poincaré inequality

$$\int_{\mathbb{R}^3}|\nabla\times\widetilde{A}|^2 = \int_{\mathbb{R}^3}|\nabla\otimes\widetilde{A}|^2 \leq C\int_{B(2\ell)}|\nabla\otimes A|^2 + C\ell^{-2}\int_{B(2\ell)}|A - \langle A\rangle|^2 \leq C\int_{B(2\ell)}|\nabla\otimes A|^2.$$

Combining this with (5.7) we obtain (5.6). $\square$

We return to the estimate of $\mathcal{T}_k^{(2)}(A)$, and shifting r_k to the origin and using (5.6) we obtain

$$\begin{aligned}\mathcal{T}_k^{(2)}(A) \geq & - C\varepsilon h^{-3}\int_{|x|\leq r}\Big(\varepsilon^{-1}\big[h^2r^{-2} + r_{min}^{-1} + 1\big]\Big)^{5/2} - C\varepsilon\int_{|x|\leq r}\Big(\varepsilon^{-1}\big[h^2r^{-2} + r_{min}^{-1} + 1\big]\Big)^4 \\ \geq & - C\varepsilon^{-3/2}h^{-3}\Big(h^5r^{-2} + r^3\Big) - C\varepsilon^{-3}\Big(h^8r^{-5} + r^3\Big) \geq -C\varepsilon^{-3/2}h^{-3\xi} - C\varepsilon^{-3}h^{3-3\xi}\end{aligned}$$

with a constant C depending on κ_0 and r_{min}. This error term is of order $o(h^2)$ as long as $\varepsilon \geq h$ and $\xi < 1/6$, which we will assume from now on.

Finally, for the term $\mathcal{T}_k^{(3)}$, after shifting, rescaling and using $z_k \leq 1$

$$\inf_A \mathcal{T}_k^{(3)}(A) \geq \varepsilon \inf_A \left\{\mathrm{Tr}\,\Big[\theta_d\big(T_{h=1}(A) - \frac{2h^{-1}}{|x|}\big)\theta_d\Big] + \frac{1}{4\kappa h}\int_{B(2d)}|\nabla\otimes A|^2\right\}$$

with $d := rh^{-1} = h^{-\xi}$ and $\theta_d(x) = \theta_-(x/d)$. Now we will use the "running energy scale" argument as in the proof of Lemma 2.1 of [ES3], where $2h^{-1}$ plays the role of Z in Lemma 2.1 of [ES3], the localization errors in (2.14) of [ES3] are not present, and the key condition in [ES3] that $Z\alpha^2$ is sufficiently small translates into κ being sufficiently small. Using the final result (3.23) from [ES3], and noting that the d^{-2} term there was due to the localization error that is not present now, we obtain

$$\inf_A \mathcal{T}_k^{(3)}(A) \geq -C\varepsilon h^{-5/2} d^{1/2}, \tag{5.8}$$

which if $o(h^{-2})$ provided $\varepsilon \ll h^{(\xi+1)/2}$. These constraints, together with the previous conditions $\varepsilon r^{1/2} \ll h$, $\varepsilon \geq h$ and $\xi < 1/6$ leave plenty of room, choosing for example $\xi = \frac{1}{10}$ and $\varepsilon = h^{3/4}$. In summary, for the first line in (5.4) we proved that

$$\inf_A \sum_{k=1}^M \mathcal{T}_k(A) \geq \sum_{k=1}^M \left[2(2\pi h)^{-3} \int_{\mathbb{R}^3\times\mathbb{R}^3} \theta_{r,k}^2 \left[p^2 - \frac{z_k}{|q-r_k|} \right]_- \mathrm{d}q\mathrm{d}p + 2h^{-2} z_k^2 S(z_k\kappa) \right] + o(h^{-2}). \tag{5.9}$$

Second line in (5.4)

By the magnetic Lieb-Thirring inequality from (5.6) we have

$$\begin{aligned} \mathrm{Tr}\,&\Big[\Phi_+\big(T_h(A) - V - Ch^2 W_R\big)\Phi_+\Big]_- + \frac{\varepsilon}{2\kappa h^2}\int |\nabla\otimes A|^2 \\ &\geq -Ch^{-3}\int_{\Omega_+} [V + Ch^2 W_R]_+^{5/2} - C\kappa^3\varepsilon^{-3}\int_{\Omega_+} [V + Ch^2 W_R]_+^4, \end{aligned} \tag{5.10}$$

where $\Omega_+ := \mathrm{supp}\Phi_+$. The contribution of the W_R terms is negligible using $\|W_R\|_\infty \leq CR^{-2}$: and that its support has a volume CR^3:

$$h^{-3}\int [h^2 W_R]^{5/2} + \kappa^3\varepsilon^{-3}\int [h^2 W_R]^4 \leq Ch^2 R^{-2} + C\kappa_0^3 \varepsilon^{-3} h^8 R^{-5} \leq \begin{cases} Ch^3 & \text{if } \mu = 0 \\ Ch^2 & \text{if } \mu \neq 0 \end{cases}$$

with a constant that may depend on μ. The positive part of the potential $[V(x)]_+$ is zero for $\mu \neq 0$ in Ω_+ and it can be estimated by $f(x)^2 \leq d(x)^{-4}$ according to (2.16) if $\mu = 0$, so

$$\int_{\Omega_+} \left(h^{-3}[V+\mu]_+^{5/2} + \kappa^3\varepsilon^{-3}[V+\mu]_+^4 \right) \leq \begin{cases} C(h^{-3}R^{-7} + \varepsilon^{-3}R^{-13}) & \text{if } \mu = 0 \\ 0 & \text{if } \mu \neq 0 \end{cases}$$

with a constant depending on κ_0 and M. With the choice of (5.1) and recalling $\varepsilon \geq h$, the lower bound on the second line in (5.4) thus vanishes as $h \to 0$.

Third line in (5.4)

This estimate will be very similar to the proof of Lemma 4.1, so we will skip some details here. We choose $\ell(u) = \ell_u := \frac{1}{100}\sqrt{r^2 + d(u)^2}$ and $f_u = \min\{\ell_u^{-1/2}, \ell_u^{-2}\}$ for the scaling functions and define the regime

$$\mathcal{Q} := \{x \ : \ |x| \le 2R,\ |x - r_k| \ge r/3,\ k = 1, 2, \dots, M\} \tag{5.11}$$

which supports $\Phi_-\phi_+$. Inserting the partition of unity (2.2) and reallocating the localization error, we have

$$\begin{aligned}\operatorname{Tr}\Big[\Phi_-\phi_+\big(T_h(A) - V - Ch^2 W_{r,R}\big)\phi_+\Phi_-\Big]_- &+ \frac{1}{8\kappa h^2}\int_{\mathbb{R}^3\setminus\bigcup_k B_{r_k}(r/4)} |\nabla\otimes A|^2 \\ &\ge \int_{\mathcal{Q}} \frac{\mathrm{d}u}{\ell_u^3}\mathcal{E}(A, V_u^+, \psi_u),\end{aligned} \tag{5.12}$$

where we defined

$$\mathcal{E}(A, U, \psi_u) := \operatorname{Tr}\Big[\psi_u\Phi_-\phi_+\Big(T_h(A) - U\Big)\phi_+\Phi_-\psi_u\Big]_- + \frac{c}{\kappa h^2}\int_{B_u(2\ell_u)} |\nabla\otimes A|^2$$

for any potential U and with some sufficiently small positive universal constant $c > 0$, and we defined

$$V_u^+(x) := V(x) + Ch^2\big(W_{r,R}(x) + |\nabla\psi_u(x)|^2\big)$$

on the support of ψ_u. We recall from (2.16) that $V(x) \le Cf(x)^2 \le Cf_u^2$ on the support of ψ_u, since $f(x)$, defined in (2.15), is comparable with f_u. Thus

$$|V_u^+(x)| \le Cf_u^2 + Ch^2\ell_u^{-2} \le Cf_u^2 \le Cf(x)^2, \qquad \text{on supp}\ \psi_u,$$

where we distinguished the case $\mu = 0$ and $\mu \ne 0$. In the latter case $|u|$ is bounded (depending on μ) and thus f_u is bounded from below. We also used that $h \le C\ell_u f_u = C\min\{\ell_u^{1/2}, \ell_u^{-1}\}$, which holds since ℓ_u is between a constant multiple of r and R if $u \in \mathcal{Q}$. Similar estimate holds for the derivatives of V_u^+, i.e. the main condition (2.7) of Theorem 2.2 is satisfied for V_u^+ with scaling functions $\ell = \ell_u$ and $f = f_u$. The other condition, $\kappa \le \kappa_0 f_u^{-2}\ell_u^{-1}$, is trivially satisfied. Applying Theorem 2.2, we get from (5.12) that

$$\begin{aligned}\inf_A &\left[\operatorname{Tr}\Big[\Phi_-\phi_+\big(T_h(A) - V - Ch^2 W_{r,R}\big)\phi_+\Phi_-\Big]_- + \frac{1}{8\kappa h^2}\int_{\mathbb{R}^3\setminus\bigcup_k B_{r_k}(r/4)} |\nabla\otimes A|^2\right] \\ &\ge \int_{\mathcal{Q}} \frac{\mathrm{d}u}{\ell_u^3}\left\{2(2\pi h)^{-3}\iint \big[(\psi_u\Phi_-\phi_+)(q)\big]^2\big[p^2 - V_u^+(q)\big]_- \mathrm{d}q\mathrm{d}p - Ch^{-2+\varepsilon}f_u^{4-\varepsilon}\ell_u^{2-\varepsilon}\right\} \\ &= \int_{\mathcal{Q}} \frac{\mathrm{d}u}{\ell_u^3}\left\{ -2(2\pi h)^{-3}\frac{8\pi}{15}\int \big[(\psi_u\Phi_-\phi_+)(q)\big]^2\big[V_u^+(q)\big]_+^{5/2}\mathrm{d}q\right\} - Ch^{-2+\varepsilon}\int_{\mathcal{Q}}\frac{\mathrm{d}u}{\ell_u^3}f_u^{4-\varepsilon}\ell_u^{2-\varepsilon}.\end{aligned}$$

The second term is $O(h^{-2+\varepsilon})$ since the integral is finite even after extending to $\mathbb{R}^3$ from $\mathcal{Q}$. In the first term we use that the localization errors in V_u^+ are bounded by $Ch^2\ell_u^{-2} \le Ch^2[d(x)+r]^{-2}$ and are supported in a ball of radius CR, and thus

$$
\begin{aligned}
h^{-3}\int(\psi_u\Phi_-\phi_+)^2[V_u^+]_+^{5/2} \le& (1+\varepsilon)h^{-3}\int(\psi_u\Phi_-\phi_+)^2[V]_+^{5/2} + C\varepsilon^{-3/2}h^{-3}\int_{|x|\le CR}\Big[\frac{h^2}{d(x)+r}\Big]^{5/2}\mathrm{d}x \\
\le& h^{-3}\int(\psi_u\Phi_-\phi_+)^2[V]_+^{5/2} + C\varepsilon h^{-3} + C\varepsilon^{-3/2}h^2R^{1/2} \qquad (5.13)
\end{aligned}
$$

since $|V| \le f^2 \in L^{5/2}$. Choosing $\varepsilon = h^{1+\zeta}$ with a small $\zeta > 0$, and recalling that $R \le Ch^{-1/2}$, we obtain that the two error terms are of order $h^{-2+\zeta}$, which even after the $\int_{\mathcal{Q}}\ell_u^{-3}\mathrm{d}u$ integration is $o(h^{-2})$.

In the main term, we perform the $\mathrm{d}u$ integration and use (2.2) to obtain

$$
\text{Third line of (5.4)} \ge 2(2\pi h)^{-3}\iint\big[(\Phi_-\phi_+)(q)\big]^2\big[p^2 - V(q)\big]_-\mathrm{d}q\mathrm{d}p - o(h^{-2}).
$$

Collecting the estimates of all three terms in (5.4) and using the properties of the cutoff functions, we have

$$
\begin{aligned}
&\mathrm{Tr}\,[T_h(A) - V]_- + \frac{1}{\kappa h^2}\int_{\mathbb{R}^3}|\nabla\otimes A|^2 \\
&\quad\ge 2(2\pi h)^{-3}\iint\big[p^2 - V(q)\big]_-\mathrm{d}q\mathrm{d}p + 2h^{-2}\sum_{k=1}^{M}z_k^2 S(z_k\kappa) \\
&\qquad + 2(2\pi h)^{-3}\iint\Phi_+(q)^2\big[p^2 - V(q)\big]_-\mathrm{d}q\mathrm{d}p \\
&\qquad + 2(2\pi h)^{-3}\sum_{k=1}^{M}\iint\theta_{r,k}^2\left(\Big[p^2 - \frac{z_k}{|q-r_k|}\Big]_- - \Big[p^2 - V(q)\Big]_-\right)\mathrm{d}q\mathrm{d}p - o(h^{-2}). \qquad (5.14)
\end{aligned}
$$

The middle term in the r.h.s. in absolute value is bounded by

$$
Ch^{-3}\int_{|x|\ge R/2}[V]_+^{5/2} \le \begin{cases} Ch^{-3}\int_{|x|\ge R/2}d(x)^{-10} \le Ch^{-3}R^7 \le Ch^{1/2} & \text{if } \mu = 0 \\ 0 & \text{if } \mu \ne 0. \end{cases}
$$

The last term in (5.14), also in absolute value, is bounded by

$$
Ch^{-3}\sum_{k=1}^{M}\int\theta_{r,k}^2\left|\Big[\frac{z_k}{|q-r_k|}\Big]^{5/2} - [V(q)]_+^{5/2}\right|\mathrm{d}q \le Ch^{-3}\int_{|q|\le r}|q|^{-3/2}\mathrm{d}q = Ch^{-3}r^{3/2}
$$

by using (2.17), where C depends on M and r_{min}. With our choice of $r = h^{1-\frac{1}{10}}$, this error term is also negligible. This completes the proof of the lower bound in Theorem 2.7.

5.2 Upper bound

We again set $\ell_u = \frac{1}{100}\sqrt{r^2 + d(u)^2}$ and consider the appropriate cutoff functions ψ_u from (2.2). We construct a trial density matrix of the form

$$\gamma = \sum_{k=1}^{M} \theta_{r,k}\gamma_k\theta_{r,k} + \int_{\mathcal{Q}} \frac{\mathrm{d}u}{\ell_u^3}\phi_+\psi_u\gamma_u\psi_u\phi_+, \tag{5.15}$$

where $\mathcal{Q}$ was defined in (5.11) and γ_k and γ_u are density matrices to be determined below. Since

$$\sum_k \theta_{r,k}^2 + \phi_+^2 = \phi_-^2 + \phi_+^2 = 1,$$

we obtain from (2.2) that γ is a density matrix.

5.2.1 Trial density near the nuclei

To construct γ_k, we fix some $\eta > 0$ and we notice that from the last part of Theorem 2.4, for any unscaled cutoff function ϕ, there exists some $R(\eta)$ such that for any $R_0 > R(\eta)$ there is a vector potential A_0, supported in $B(R_0/4)$, and there is a density matrix $\widehat{\gamma}$ such that

$$\begin{aligned}\operatorname{Tr}\Big[\widehat{\gamma}\phi_{R_0}\Big(T_{h=1}(A_0) - \frac{1}{|x|}\Big)\phi_{R_0}\Big] + \frac{1}{z_k\kappa}\int |\nabla\otimes A_0|^2 \\ - 2(2\pi)^{-3}\int_{\mathbb{R}^3\times\mathbb{R}^3} \phi_{R_0}^2(q)\Big[p^2 - \frac{1}{|q|}\Big]_- \mathrm{d}p\mathrm{d}q \le 2S(z_k\kappa) + \eta.\end{aligned} \tag{5.16}$$

We can also assume that

$$\operatorname{Tr}\Big[\widehat{\gamma}\phi_{R_0}\Big(T_{h=1}(A_0) - \frac{1}{|x|}\Big)\phi_{R_0}\Big] + \frac{1}{z_k\kappa}\int |\nabla\otimes A_0|^2 \le 0 \tag{5.17}$$

by noticing that the semiclassical integral is of order $R_0^{1/2}$ which dominates over the $2S(z_k\kappa)+\eta$ term for sufficiently large R_0.

Fixing an appropriately large R_0, γ_k and A_k are now obtained from $\widehat{\gamma}$ and A_0 by shifting and rescaling, such that

$$\begin{aligned}\operatorname{Tr}\Big[\gamma_k\theta_{r,k}\Big(T_h(A_k) - \frac{z_k}{|x-r_k|}\Big)\theta_{r,k}\Big] + \frac{1}{\kappa h^2}\int |\nabla\otimes A_k|^2 \\ - 2(2\pi h)^{-3}\int_{\mathbb{R}^3\times\mathbb{R}^3} \theta_{r,k}^2(q)\Big[p^2 - \frac{z_k}{|q-r_k|}\Big]_- \mathrm{d}p\mathrm{d}q \le 2h^{-2}z_k^2 S(z_k\kappa) + Ch^{-2}\eta\end{aligned} \tag{5.18}$$

with $r = R_0 h^2 z_k^{-1}$. Here we used that the unscaled cutoff function ϕ can be chosen to be $\phi(x) = \theta_-(d(x))$ so that after rescaling and shift ϕ_{R_0} became $\theta_{r,k}$. We choose $R_0 = h^{-1-\xi}z_k$

such that $r = h^{1-\xi}$ and clearly $R_0 > R(\eta)$ is satisfied in the limit as $h \to 0$. We also remark that A_k is supported in $B_{r/4}(r_k)$ which are disjoint balls for different k's. Defining $A := \sum_{k=1}^{M} A_k$, we have $A = A_k$ in the support of $\theta_{r,k}$. Thus summing up (5.18), and using that the replacement of $z_k|q-r_k|^{-1}$ with $V(q)$ in the semiclassical integral term is negligible (see the estimate of the last term in (5.14)), we have

$$\sum_{k=1}^{M} \mathrm{Tr}\left[\gamma_k\theta_{r,k}\Big(T_h(A) - \frac{z_k}{|x-r_k|}\Big)\theta_{r,k}\right] + \frac{1}{\kappa h^2}\int |\nabla\otimes A|^2$$
$$\leq 2(2\pi h)^{-3}\int_{\mathbb{R}^3\times\mathbb{R}^3} \phi_-^2(q)\Big[p^2 - V(q)\Big]_- \mathrm{d}p\mathrm{d}q + 2h^{-2}\sum_{k=1}^{M} z_k^2 S(z_k\kappa) + Ch^{-2}\eta. \quad (5.19)$$

Now we establish some properties of the density $\varrho_k(x) := \gamma_k(x,x)$. Similarly to the estimate $\mathcal{T}_k^{(3)}(A)$ from (5.8), we have for any $L > 0$

$$\inf_A \left\{ \mathrm{Tr}\left[\phi_L\Big(T_h(A) - \frac{2}{|x-y|}\Big)\phi_L\right]_- + \frac{1}{\kappa h^2}\int |\nabla\otimes A|^2 \right\} \geq -Ch^{-3}L^{1/2}$$

uniformly for any $y \in \mathbb{R}^3$ if κ is sufficiently small. In particular, for any density matrix γ with density ϱ_γ we have

$$2\sup_{y\in\mathbb{R}^3}\int \phi_L^2(x)\frac{\varrho_\gamma(x)}{|x-y|}\mathrm{d}x \leq Ch^{-3}L^{1/2} + \mathrm{Tr}\,\gamma\phi_L T_h(A)\phi_L + \frac{1}{\kappa h^2}\int |\nabla\otimes A|^2$$

for any vector potential A and thus

$$\sup_{y\in\mathbb{R}^3}\int \phi_L^2(x)\frac{\varrho_\gamma(x)}{|x-y|}\mathrm{d}x \leq Ch^{-3}L^{1/2} + \inf_A\left\{\mathrm{Tr}\left[\gamma\phi_L\Big(T_h(A) - \frac{1}{|x|}\Big)\phi_L\right] + \frac{1}{\kappa h^2}\int |\nabla\otimes A|^2\right\}.$$

Applying this bound to $\widehat{\gamma}$ constructed above (with $L = R_0$, $h = 1$ and $A = A_0$) and using (5.17), we have

$$\sup_{y\in\mathbb{R}^3}\int \phi_{R_0}^2(x)\frac{\varrho_{\widehat{\gamma}}(x)}{|x-y|}\mathrm{d}x \leq CR_0^{1/2}$$

which, after rescaling and shifting $\widehat{\gamma}$ to γ_k amounts to

$$\sup_{y\in\mathbb{R}^3}\int \theta_{r,k}^2(x)\frac{\varrho_{\gamma_k}(x)}{|x-y|}\mathrm{d}x \leq Ch^{-3}r^{1/2}. \quad (5.20)$$

In particular,

$$\int \theta_{r,k}^2(x)\varrho_{\gamma_k}(x)\mathrm{d}x \leq Ch^{-3}r^{3/2} \quad (5.21)$$

by choosing $y = r_k$ and using that $|x - r_k| \leq Cr$ on the support of $\theta_{r,k}$.

Combining (5.21) with (2.17) we see that $z_k|x - r_k|^{-1}$ can be replaced with V in the l.h.s. of (5.19) at an error of order $h^{-3}r^{3/2} = o(h^{-2})$ and thus we have

$$\sum_{k=1}^{M} \mathrm{Tr}\left[\gamma_k\theta_{r,k}\Big(T_h(A) - V\Big)\theta_{r,k}\right] + \frac{1}{\kappa h^2}\int|\nabla\otimes A|^2$$

$$\leq 2(2\pi h)^{-3}\int_{\mathbb{R}^3\times\mathbb{R}^3}\phi_-^2(q)\Big[p^2 - V(q)\Big]_-\mathrm{d}p\mathrm{d}q + 2h^{-2}\sum_{k=1}^{M} z_k^2 S(z_k\kappa) + Ch^{-2}\eta. \quad (5.22)$$

Moreover, it follows from (5.20) and (5.21) that the density $\theta_{r,k}^2\varrho_{\gamma_k}$ of the density matrix $\theta_{r,k}\gamma_k\theta_{r,k}$ satisfies

$$D(\theta_{r,k}^2\varrho_{\gamma_k}) = \frac{1}{2}\iint \theta_{r,k}(x)^2\theta_{r,k}(y)^2\frac{\varrho_{\gamma_k}(x)\varrho_{\gamma_k}(y)}{|x-y|}\mathrm{d}x\mathrm{d}y \leq Ch^{-6}r^2. \quad (5.23)$$

5.2.2 Trial density away from the nuclei

Now we construct γ_u for any $u \in \mathcal{Q}$. Since supp $A_k \subset B_{r/4}(r_k)$ and $\phi_+(x)$ is supported at $d(x) \geq r/2$, thus on the support of ϕ_+ we have $A = 0$. Therefore it is sufficient to construct a non-magnetic trial state γ_u within each ball $B_u(\ell_u)$ which supports ψ_u. This was achieved in Corollary 15 of [SS] and we just quote the relevant upper bound (we formulate it particles with spin, this accounts for an additional factor 2 compared with [SS]):

Proposition 5.3. *[SS, Corollary 15] Let $\chi \in C_0^7(\mathbb{R}^3)$ be supported in B_ℓ with some $\ell > 0$ and let $V \in C^3(\overline{B_\ell})$ be a real potential. Assume that for any multiindex $n \in \mathbb{N}^3$ with $|n| \leq 7$ we have*

$$\|\partial^n\chi\|_\infty \leq C_n\ell^{-|n|}, \qquad \|\partial^n V\|_\infty \leq C_n f^2\ell^{-|n|} \quad (5.24)$$

with some constant f. Then there exists a density matrix γ such that

$$\mathrm{Tr}\left[\gamma\chi(-h^2\Delta - V)\chi\right] \leq 2(2\pi h)^{-3}\iint \chi(q)^2[p^2 - V(q)]_-\mathrm{d}p\mathrm{d}q + Ch^{-3+6/5}f^{3+4/5}\ell^{3-6/5},$$

where C depends only on the constants in (5.24). Moreover, the density $\varrho_\gamma(x)$ of γ satisfies

$$\Big|\varrho_\gamma(x) - 2(2\pi h)^{-3}\omega_3[V(x)]_+^{3/2}\Big| \leq Ch^{-3+9/10}f^{3-9/10}\ell^{-9/10}, \quad (5.25)$$

for almost all $x \in B_\ell$, and

$$\Big|\int\chi^2\varrho_\gamma - 2(2\pi h)^{-3}\omega_3\int\chi^2[V]_+^{3/2}\Big| \leq Ch^{-3+6/5}, \quad (5.26)$$

where $\omega_3 = 4\pi/3$ is the volume of the unit ball.

We will apply this Proposition for each ball $B_u(\ell_u)$ and with $\chi := \phi_+\psi_u$. From (2.3) and (2.16) it is easy to see that the conditions (5.24) are satisfied with our choice of $\ell = \ell_u = \frac{1}{100}\sqrt{r^2+d(u)^2}$ and $f_u = f(u) = \min\{d(u)^{-1/2}, d(u)^{-2}\}$ as given in (2.15). The density matrix thus constructed in Proposition 5.3 will be denoted by γ_u and this will be the density matrix in (5.15). With this choice we have

$$
\begin{aligned}
&\mathrm{Tr}\left[(-h^2\Delta - V)\int_{\mathcal{Q}}\frac{\mathrm{d}u}{\ell_u^3}\phi_+\psi_u\gamma_u\psi_u\phi_+\right] \\
&\quad\leq 2(2\pi h)^{-3}\int_{\mathcal{Q}}\frac{\mathrm{d}u}{\ell_u^3}\iint \phi_+(q)^2\psi_u(q)^2[p^2-V(q)]_-\mathrm{d}p\mathrm{d}q + Ch^{-3+6/5}\int_{\mathcal{Q}}\frac{\mathrm{d}u}{\ell_u^3}f_u^{3+4/5}\ell_u^{3-6/5} \\
&\quad\leq 2(2\pi h)^{-3}\iint \phi_+(q)^2[p^2-V(q)]_-\mathrm{d}p\mathrm{d}q + Ch^{-2+1/5}\int_{\mathcal{Q}}\frac{\mathrm{d}u}{\ell_u^3}f_u^{3+4/5}\ell_u^{3-6/5}. \qquad (5.27)
\end{aligned}
$$

The error term can easily be computed by using that $\ell_u \sim d(u)$ for $u \in \mathcal{Q}$ as

$$
\begin{aligned}
\int_{\mathcal{Q}}\frac{\mathrm{d}u}{\ell_u^3}f_u^{3+4/5}\ell_u^{3-6/5} &\leq C\int_{r/3\leq d(u)\leq 1} d(u)^{-19/10-6/5}\mathrm{d}u + C\int_{1\leq d(u)\leq 2R} d(u)^{-38/5-6/5}\mathrm{d}u \\
&\leq Cr^{-1/10} + C. \qquad (5.28)
\end{aligned}
$$

Since $r \geq h$, we have $h^{1/5}r^{-1/10} \leq h^{1/10}$, so the error term in (5.27) is $o(h^{-2})$.

We now use γ from (5.15) and $A = \sum_k A_k$ constructed in Section 5.2.1 to complete the proof of the upper bound (2.21) in Theorem 2.7. Combining (5.22) and (5.27) and recalling that A and ϕ_+ are supported disjointly, we have

$$
\begin{aligned}
&\mathrm{Tr}\,[T_h(A) - V]\gamma + \frac{1}{\kappa h^2}\int |\nabla\otimes A|^2 \\
&\qquad \leq 2(2\pi h)^{-3}\iint \left[p^2 - V(q)\right]_-\mathrm{d}q\mathrm{d}p + 2h^{-2}\sum_{k=1}^M z_k^2 S(z_k\kappa) + o(h^{-2}) + Ch^{-2}\eta,
\end{aligned}
$$

where we also used that $\phi_+^2 + \phi_-^2 = 1$. Finally, letting $h \to 0$ first and then $\eta \to 0$, we obtain the upper bound in (2.18) and (2.21).

To complete the proof of Theorem 2.7, it remains to prove (2.19) and (2.20). From (5.15) we have

$$
\varrho_\gamma = \sum_{k=1}^M \theta_{r,k}^2\varrho_{\gamma_k} + \int_{\mathcal{Q}}\frac{\mathrm{d}u}{\ell_u^3}\psi_u^2\phi_+^2\varrho_{\gamma_u}.
$$

Using (5.21) and $\phi_+ \leq 1$ we have

$$
\int \varrho_\gamma \leq Ch^{-3}r^{3/2} + \int_{\mathcal{Q}}\frac{\mathrm{d}u}{\ell_u^3}\int \psi_u^2\varrho_{\gamma_u}.
$$

The first term is of order $h^{-3/2(1+\xi)} = h^{-2+7/20}$, hence negligible. In the second term we use (5.26) and (2.2) to get

$$\int_{\mathcal{Q}} \frac{\mathrm{d}u}{\ell_u^3} \int \psi_u^2 \varrho_{\gamma_u} \le \frac{1}{3\pi^2 h^3} \int_{\mathcal{Q}} \frac{\mathrm{d}u}{\ell_u^3} \int \psi_u^2 [V]_+^{3/2} + Ch^{-2+1/5} \int_{\mathcal{Q}} \frac{\mathrm{d}u}{\ell_u^3}$$
$$\le \frac{1}{3\pi^2 h^3} \int [V]_+^{3/2} + Ch^{-2+1/5}(|\log r| + |\log R|). \tag{5.29}$$

Since both logarithms are of order $|\log h|$, we obtained (2.19).

To prove (2.20), we note that $\sqrt{D(\varrho)}$ satisfies the triangle inequality, thus we have

$$D\Big(\varrho_\gamma - (3\pi^2)^{-1} h^{-3} [V]_-^{3/2}\Big) \le CD\Big(\int_{\mathcal{Q}} \frac{\mathrm{d}u}{\ell_u^3} \psi_u^2 \phi_+^2 \Big[\varrho_{\gamma_u} - \frac{1}{3\pi^2 h^3}[V]_+^{3/2}\Big]\Big) \tag{5.30}$$
$$+ CD\Big(\frac{1}{3\pi^2 h^3}[V]_+^{3/2}\Big[\int_{\mathcal{Q}} \frac{\mathrm{d}u}{\ell_u^3}\psi_u^2\phi_+^2 - 1\Big]\Big) + C\sum_k D(\varrho_{\gamma_k}).$$

The last term is smaller than $O(h^{-5+\varepsilon})$ with some small ε by using (5.23). For the second term in (5.30) we note that by (2.2)

$$\Big|\int_{\mathcal{Q}} \frac{\mathrm{d}u}{\ell_u^3}\psi_u(x)^2\phi_+(x)^2 - 1\Big| \le |\phi_+(x)^2 - 1| + \int_{\mathcal{Q}^c} \frac{\mathrm{d}u}{\ell_u^3}\psi_u(x)^2 \le C\big(\mathbf{1}(d(x) \le r) + \mathbf{1}(d(x) \ge R)\big)$$

and thus

$$D\Big(\frac{1}{3\pi^2 h^3}[V]_+^{3/2}\Big[\int_{\mathcal{Q}} \frac{\mathrm{d}u}{\ell_u^3}\psi_u^2\phi_+^2 - 1\Big]\Big) \le Ch^{-6}\Big[D\Big([V]_+^{3/2}\mathbf{1}(d(x) \le r)\Big) + D\Big([V]_+^{3/2}\mathbf{1}(d(x) \ge R)\Big)\Big].$$

By the Hardy-Littlewood-Sobolev inequality we have $D(\varrho) \le C\|\varrho\|_{6/5}^2$ for any real function ϱ, therefore this error is bounded by

$$Ch^{-6}\Big(\int_{d(x)\le r}[V]_+^{9/5} + \int_{d(x)\ge R}[V]_+^{9/5}\Big)^{5/3}.$$

Using that $V(x)$ is essentially $z_k|x - r_k|^{-1}$ near the nuclei and $V(x) \sim |x|^{-4}$ for large x (see (2.16) and (2.17)), we easily obtain

$$D\Big(\frac{1}{3\pi^2 h^3}[V]_+^{3/2}\Big[\int_{\mathcal{Q}} \frac{\mathrm{d}u}{\ell_u^3}\psi_u^2\phi_+^2 - 1\Big]\Big) \le Ch^{-6}\big(r^2 + R^{-7}\big)$$

which is smaller than $O(h^{-5+\varepsilon})$.

Finally, we estimate the first term on the r.h.s. of (5.30). By the Hardy-Littlewood-Sobolev inequality and (5.25)

$$\begin{aligned} D\Big(\int_{\mathcal{Q}}\frac{\mathrm{d}u}{\ell_u^3}\psi_u^2\phi_+^2\Big[\varrho_{\gamma_u}-\frac{1}{3\pi^2h^3}[V]_+^{3/2}\Big]\Big)^{1/2} \leq & C\Big\|\int_{\mathcal{Q}}\frac{\mathrm{d}u}{\ell_u^3}\psi_u^2\phi_+^2\Big[\varrho_{\gamma_u}-\frac{1}{3\pi^2h^3}[V]_+^{3/2}\Big]\Big\|_{6/5} \\ \leq & \int_{\mathcal{Q}}\frac{\mathrm{d}u}{\ell_u^3}\Big\|\psi_u^2\phi_+^2\Big[\varrho_{\gamma_u}-\frac{1}{3\pi^2h^3}[V]_+^{3/2}\Big]\Big\|_{6/5} \\ \leq & Ch^{-2-\frac{1}{10}}\int_{\mathcal{Q}}\frac{\mathrm{d}u}{\ell_u^3}f_u^{21/10}\ell_u^{8/5} \\ \leq & Ch^{-2-\frac{1}{10}} \end{aligned} \tag{5.31}$$

as the last integral is bounded. In the second line we estimated

$$\Big\|\psi_u^2\phi_+^2\Big[\varrho_{\gamma_u}-\frac{1}{3\pi^2h^3}[V]_+^{3/2}\Big]\Big\|_{6/5} \leq Ch^{-2-\frac{1}{10}}f_u^{21/10}\ell_u^{8/5}$$

by using (5.25) and (2.3). This completes the proof of (2.20) and the proof of Theorem 2.7. □

6 Equivalence of the two definitions of $S(\kappa)$

Proof of Lemma 2.5. Setting $h=\nu^{1/2}$, after a change of variables we have

$$\frac{2}{(2\pi)^3}\int_{\mathbb{R}^3\times\mathbb{R}^3}\Big[p^2-\frac{1}{|q|}+\nu\Big]_-\mathrm{d}p\mathrm{d}q=\nu\frac{2}{(2\pi h)^3}\int_{\mathbb{R}^3\times\mathbb{R}^3}\Big[p^2-\frac{1}{|q|}+1\Big]_-\mathrm{d}p\mathrm{d}q.$$

Similarly, by a simple rescaling, $x\to\nu^{-1}x$ we get

$$\inf_A\Big\{\mathrm{Tr}\,\Big[T_1(A)-\frac{1}{|x|}+\nu\Big]_-+\frac{1}{\kappa}\int_{\mathbb{R}^3}|\nabla\otimes A|^2\Big\}=\nu\inf_A\Big\{\mathrm{Tr}\,\Big[T_{\nu^{1/2}}(A)-\frac{1}{|x|}+1\Big]_-+\frac{1}{\kappa\nu}\int_{\mathbb{R}^3}|\nabla\otimes A|^2\Big\}.$$

We apply Theorem 2.7 to the potential $V(x)=|x|^{-1}-1$ and with $h=\nu^{1/2}$. Notice that $V(x)$ satisfies the conditions (2.16) and (2.17) with $\mu=1$, $M=1$, $r_{min}=\infty$, $z_1=1$ and $r_1=0$. We get

$$\inf_A\Big\{\mathrm{Tr}\,\Big[T_1(A)-\frac{1}{|x|}+\nu\Big]_-+\frac{1}{\kappa}\int_{\mathbb{R}^3}|\nabla\otimes A|^2\Big\}-\frac{2}{(2\pi)^3}\int_{\mathbb{R}^3\times\mathbb{R}^3}\Big[p^2-\frac{1}{|q|}+\nu\Big]_-\mathrm{d}p\mathrm{d}q=2S(\kappa)+O(\nu^{\varepsilon/2})$$

which proves (2.14). □

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